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(SSR129): Final Report

Author(s): Veirs, Douglas Kirk
Stroud, Mary Ann
Martinez, Max
Carrillo, Alex
Berg, John M.
Narlesky, Joshua Edward
Worl, Laura Ann

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MIS High-Purity Plutonium/Uranium Oxide Hydride Product 5501407 (SSR129): Final Report

Authors:

D. Kirk Veirs
Mary A. Stroud
Max A. Martinez (retired)
Alex Carrillo (retired)
John M. Berg
Joshua E. Narlesky
Laura Worl

MIS High-Purity Plutonium/Uranium Oxide Hydride Product 5501579 (SSR129): Final Report

Abstract

A high-purity uranium/plutonium mixed oxide material from the Material Identification and Surveillance (MIS) Program inventory has been studied with regard to gas generation and corrosion in a storage environment. Sample 5501579 represents process plutonium oxides from high purity mixed oxides and mixed oxides from alloy oxidation at Hanford, hydride oxide from Rocky Flats, and mixed oxides from alloy oxidation and scrap mixed oxides at Savannah River that are currently stored in 3013 containers. This study followed over time the gas pressure of two samples of this material with nominally 0.5 wt% water in a sealed container with an internal volume scaled to 1/500th of the volume of a 3013 container. The first experiment studied a mixture of 60% as-received material (AR) and 40% material that had been calcined at 950 °C. The mixture contained 66% weapons grade plutonium and 11% uranium, with approximately 7.3% impurities and the remainder principally oxygen. A second experiment studied material calcined at 950 °C which contained approximately 4.3% impurities and similar uranium and plutonium content. Gas compositions were measured periodically over approximately 3.5 years in the first container and 20 months for the second container, which was terminated early due to an inadvertent container pumpdown. The maximum observed gas pressures were 152 kPa and 161 kPa, respectively. The increase over the initial pressures of 82 kPa and 88 kPa, respectively, was primarily due to generation of carbon dioxide and nitrogen gases. In the container with the AR/calcined mixture, a small amount of hydrogen and oxygen was generated and was consumed. In the container with calcined material only, hydrogen partial pressure of 18.9 kPa was measured. A small amount of oxygen was generated and was consumed. At the completion of the study, the internal components of both sealed containers showed signs of corrosion.

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Introduction

The Los Alamos National Laboratory (LANL) Shelf-life Surveillance project was established under the Material Identification and Surveillance (MIS) Program to identify early indications of potential failure mechanisms in 3013 containers.¹ Samples were taken from plutonium processes across the DOE complex. These “representative” materials were sent to LANL to be included in the MIS inventory. The small-scale surveillance project is designed to provide gas generation and corrosion information of the MIS represented materials under worst-case moisture loadings. This information, in combination with material characterization, allows predictions of the behavior of 3013 packaged materials stored at DOE sites. Pressure, gas compositions, and corrosion were monitored in small-scale reactors (SSRs) charged with nominally 10-gram samples of plutonium bearing materials with nominally 0.5 wt% water, the upper limit allowed by the DOE’s 3013 Standard.¹

This report discusses 5501407, a high purity uranium/plutonium dioxide material from the MIS Program inventory that originated in hydride oxidation in Building 779, Rooms 152A and 160A at the Rocky Flats Plant, later known as the Rocky Flats Environment Technology Site (RFETS). The plutonium oxide is representative of oxides generated from the following processes:²

- High Purity Mixed Oxides at Hanford
- Mixed Oxides from Alloy Oxidation at Hanford
- Hydride Oxide from Rocky Flats
- Mixed Oxides from Alloy Oxidation at Savannah River
- Scrap Mixed Oxides at Savannah River.



Figure 1. 5501407 upon arrival at LANL.

Material Characterization

Several measurements of material characteristics for the as-received (AR) material are summarized in Table 1. Part of this high-purity weapons grade uranium/plutonium oxide was calcined at 950 °C for two hours on July 7, 1997. The weight loss from calcination was 8%. Measurements of material characteristics for the calcined material are also summarized in Table 1. Two sealed SSRs were loaded with 5501407 material. The first SSR, SSR129, was a mixture of 60% AR material and 40% material calcined at 950 °C on July 7, 1997. After the sample was taken to determine the chemistry and the pycnometer density for the material in SSR129 but before it was loaded, 3% additional AR material and 2% of an unknown pure residue was added. The reported 60% AR/40% mix assumes the unknown residue was also a 40%/60% mixture. A second SSR, SSR129A, was loaded with material calcined to 950 °C, including 53% calcined on July 30, 1997 and 47% calcined on November 19, 2003.

Table 1. Material Physical Characteristics

| | AR | SSR129A Calcined (950 °C) | SSR129 Calculated Wt% Average (60% AR and 40% Calcined) |
|--|------|---------------------------------|---|
| Specific Surface Area (SSA) 5-point (m ² g ⁻¹) | 4.85 | 0.67 (0.5508, 0.7877) | 3.18 |
| Bulk Density (g cm ⁻³) | 2.31 | 2.36 | 2.33 |
| Tap Density (g cm ⁻³) | 2.95 | 3.47 | 3.31 |
| Pycnometer Density (g cm ⁻³) | N/A | N/A | 8.305* |

*measurement on material mixture before additional 2% unknown and 3% AR added

Table 2 summarizes the wt% of key elements, as well as any impurity present as 0.01 wt% or greater measured for the AR material, the calcined material and the mixture (prior to the addition of the additional AR and unknown material). The weight percents calculated for the mixture based on the AR and calcined material data are also summarized. Variation between the measured and calculated values may be due to inhomogeneity in the material. Oxygen is not measured and it is assumed to make up the difference between the sum of the weight percents of the listed elements plus plutonium and uranium and 100%. No measurements of soluble species were conducted for this material.

Table 2. Elemental weight % of impurities.

| Element | AR | SSR129A Calcined (950 °C) | SSR129* | SSR129 Calculated Wt% Average (60% AR and 40% Calcined) |
|------------------|------------|---------------------------------|---------|---|
| Aluminum | 0.01 | 0.0030 | 0.005 | .007 |
| Boron | 0.0211 | 0.0234 | 0.0011 | .02202 |
| Beryllium | .0558 | 0.0371 | 0.035 | 0.04832 |
| Calcium | 0.0081 | 0.0113 | 0.01 | 0.00938 |
| Carbon | 0.032 | 0.007 | 0.024 | 0.020 |
| Chromium | 0.1600 | 0.0995 | 0.142 | 0.1358 |
| Chloride | .1230-.307 | 0.1550 | 0.016 | 0.19 |
| Copper | 0.0240 | 0.0150 | | 0.0204 |
| Gallium | 0.7576 | 0.7668 | 0.956 | 0.76128 |
| Iron | 0.2205 | 0.1040 | 0.121 | 0.1739 |
| Magnesium | < 0.0003 | 0.0004 | 0.0061 | <0.00034 |
| Manganese | 0.0108 | 0.0088 | 0.0080 | 0.01 |
| Nickel | 4.300 | 2.8023 | 4.29 | 3.70092 |
| Phosphorus | < 0.0004 | 0.0612 | 0.987 | <0.02472 |
| Potassium | 0.0337 | 0.0326 | 0.0147 | 0.03326 |
| Silicon | <0.005 | <0.005 | 0.0297 | <0.005 |
| Sodium | < 0.0070 | 0.0080 | 0.0430 | <0.0074 |
| Sulfur | 4.0489 | 0.0028 | 0.434 | 2.43046 |
| Tantalum | 0.0100 | 0.0044 | | 0.00776 |
| Titanium | 0.7000 | 0.1466 | 0.142 | 0.47864 |
| Tungsten | 0.0200 | 0.0577 | 0.0582 | 0.03508 |
| Total Impurities | 10.6 | 4.3 | 7.3 | 8.1 |

*measured value of material before additional 2% unknown and 3% AR material added

Isotopic data from calorimetry/gamma isotopics for the mixed material in SSR129 is listed in Table 3. This material contained 65.7% Pu and 0.2% Am. Calorimetry data was not available for the calcined material in SSR129A.

Table 3. Isotopic data listed as mass fraction (g/g plutonium). Specific power is reported in mW per gram of material, not per gram of plutonium. The isotopics and wattage were measured on December 1, 2003 for the mixed SSR129 sample (AR and calcined to 950 °C) .

| Isotope | Mass Fraction (g/gPu) | Mass Fraction of plutonium (calorimetry) (g Pu/g of material) | 0.657 |
|---------|-----------------------|---|-------|
| Pu-238 | 0.0013200 | Specific Power (mW/g of material) | 1.642 |
| Pu-239 | 0.9412130 | | |
| Pu-240 | 0.0569221 | | |
| Pu-241 | 0.0014829 | | |
| Pu-242 | 0.0002500 | | |
| Am-241 | 0.0017634 | | |

The percent uranium determined from the Davies Gray assay method was 11.000% for the AR. The isotopic composition of the uranium in the AR material was 92.7% U-235 and 5.8% U-238 and 1.0% U-234. The percent uranium in the calcined material was 11.725%.

The material lost 7.7% of its weight upon calcination at 950 °C for 2 hours. Weight loss due to loss of non-actinide impurities listed in Table 2, primarily from Ni and S, is estimated to be 6.3%. Formation of U_3O_8 from UO_2 when uranium oxides are heated in air above 700 °C would result in a weight gain in the material while formation from UO_3 results in a weight loss.³ The observed weight loss on calcination suggests some of the AR material may have been present as UO_3 . The stoichiometry of the uranium oxide after calcination is important to understanding the experimental observations. Water is adsorbed by UO_3 to form a dihydrate whereas U_3O_8 adsorbs water only on the surface, resulting in much lower water adsorption.⁴ It has been reported that some UO_3 dihydrate is formed from U_3O_8 when stored in humid, room temperature atmospheres for long times.³

Expected specific wattage of mixed material loaded in SSR129 as a function of time is shown in Figure 2.

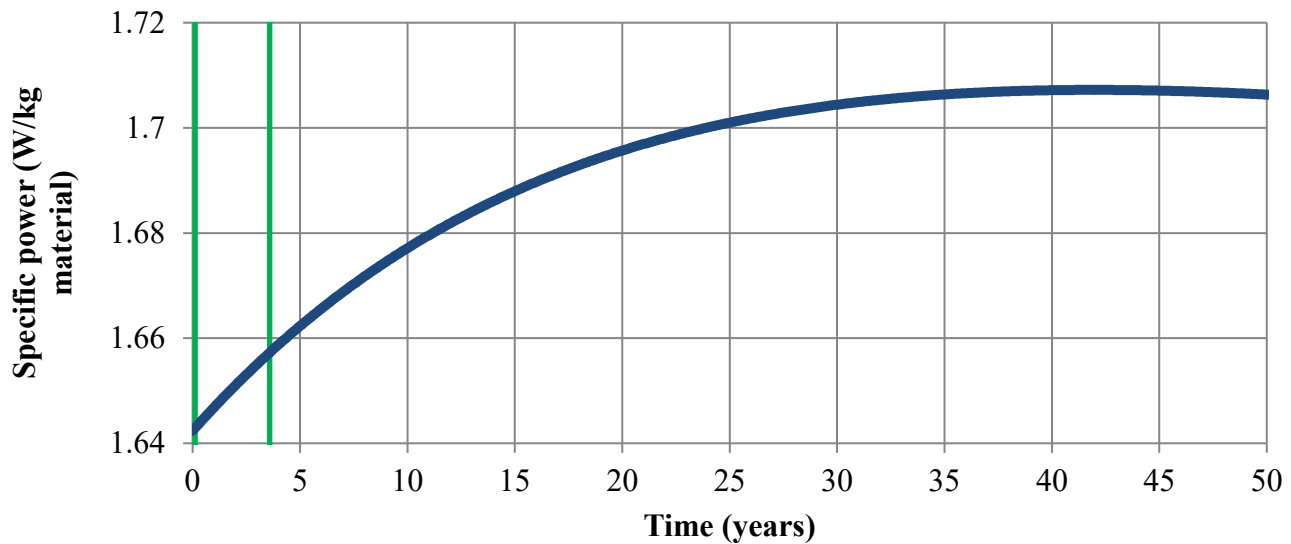


Figure 2. Expected specific wattage of 5501579 loaded in SSR129 as a function of time from the December 1, 2003 measurement. The vertical green lines bound the time the sample was in the reactor.

Figure 3 provides information on He evolution as a function of time in the mixed material in SSR129.

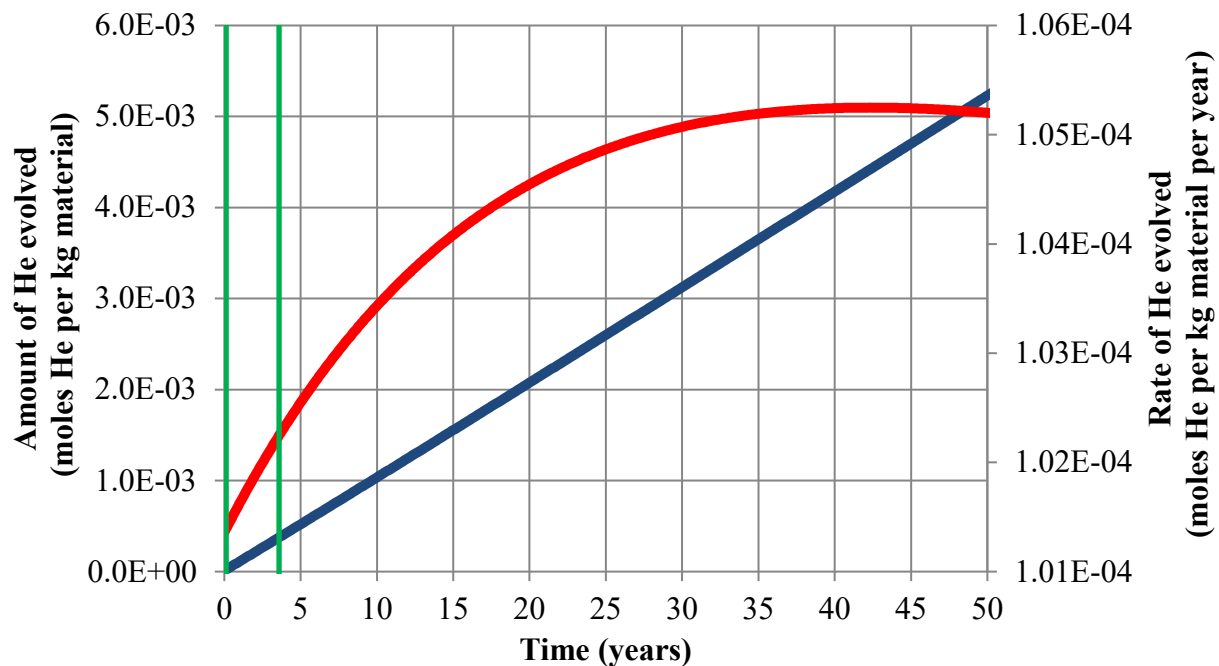


Figure 3. Integrated amount of He evolved from alpha decay from 5501579 in SSR129 as a function of time from the December 1, 2003 measurement (blue line and left axis) and the moles of He per kg material evolved per year as a function of time (red line and right axis). The vertical green lines bound the time the sample was in the reactor.

Experimental Procedure

The design of the small-scale reactor (SSR) system has been described previously.⁵ The container's nominally five cm³ internal volume is scaled to $\sim 1/500^{\text{th}}$ of the inner 3013 storage container. The material of construction of the inner small-scale containers is 304L stainless steel. The SSR consists of a container body⁶ welded into a Conflat flange and a lid consisting of a Conflat flange with tubing attachments for connections to a pressure transducer and a gas manifold. An inner bucket is used to hold material and is inserted into the container body during the loading activities. The inner bucket allows the fine plutonium oxide powder to be handled with minimal or no spillage. A low-internal-volume pressure transducer and associated low-volume tubing is attached to the lid. Small-scale reactors have interchangeable parts with varying volumes. For this study, a Type H container with a total internal volume of 5.326 cm³ was used.⁶ The gas sampling volume located between two sampling valves, 0.05 cm³ ($\sim 1\%$ of the SSR volume), allows gas composition to be determined with minimal effect on the internal gas pressure. A disassembled SSR is shown in Figure 4.

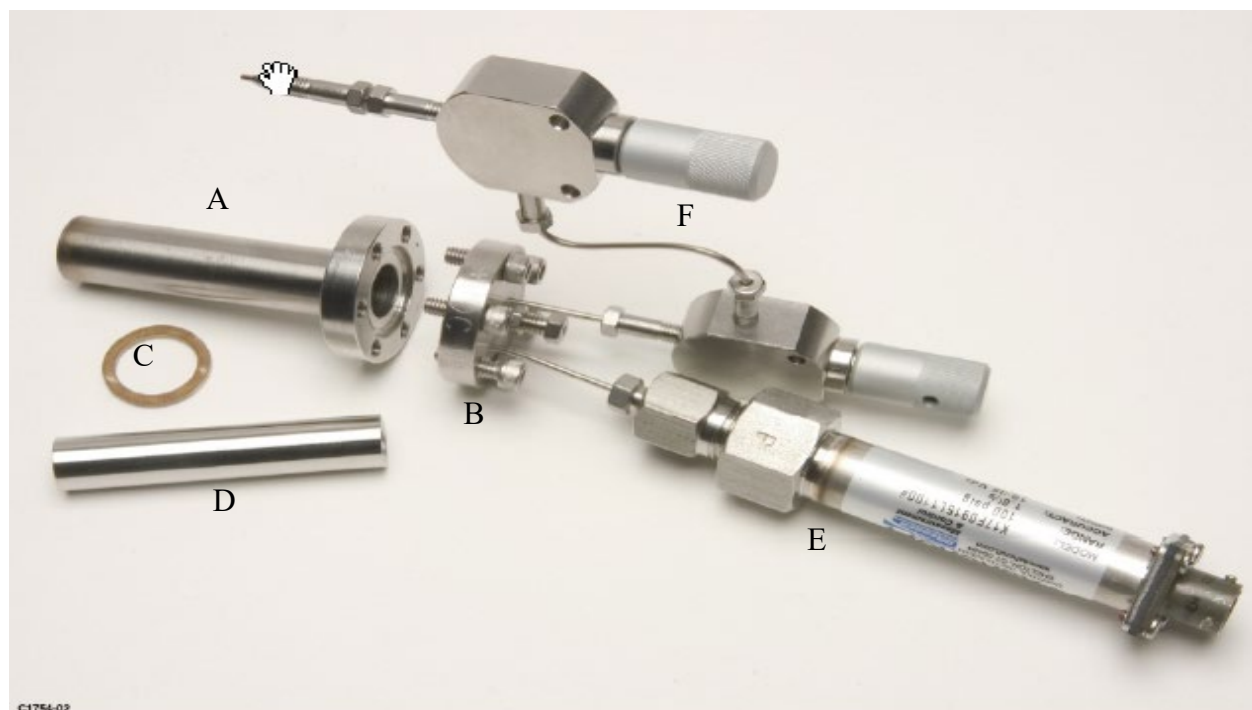


Figure 4. Disassembled SSR: Conflat container body (A) with conflat flange lid (B), copper gasket (C), inner bucket (D), pressure transducer (E), and a sampling volume between two sampling valves with connection to the gas manifold (F). Inner bucket slides into container body and holds the material.

Gas generation is characterized for each MIS represented material at the bounding moisture content of approximately 0.5 wt%. The procedure to achieve 0.5 wt% moisture included (1) estimating the moisture content of the material as it was received for small-scale loading and (2) adding sufficient water to bring the total to 0.5 wt%. The moisture content of the material was estimated by weight loss upon heating to 200 °C (LOI-200 °C) of a one gram sample that was cut from the parent lot at the same time as the 10 g small-scale sample. The LOI-200 °C samples were placed in a glass vial which remained in the glove box line with the small-scale sample until the LOI-200 °C measurement was performed, typically one day or less after the sample split and just prior to SSR loading. LOI-200 °C involved heating nominally one gram of the material for 2 hours at 200 °C, cooling the material for 10 minutes and determining the mass difference of the material before and after heating. The mass loss observed was attributed to adsorbed water. It was assumed that the LOI-200 °C material contained an additional ~1.5 monolayer (ML) equivalent of water, approximately 0.10 wt% (SSR129) and 0.02 wt% (SSR129A), as hydroxyls or chemically adsorbed water which was not removed by heating to 200 °C.⁷ The amount of water to be added to achieve 0.5 wt% total moisture was calculated as the difference between 0.5 wt% and the sum of the adsorbed water determined by LOI-200 °C and the chemically adsorbed water assumed to be 1.5 ML. In addition, a sample from the parent was split and placed in a glass vial inside of a hermetically sealed container. The water content of this sample was determined by Thermal Gravimetric Analysis-Mass Spectroscopy (TGA-MS). TGA-MS is inherently more accurate than LOI-200 °C, although there can be errors associated with this method due to handling and excessive times before the sample is run. TGA results were not available when the sample was loaded.

The procedure to add moisture is described briefly. A ten-gram sample of the 5501579 material was placed on a balance in a humidified chamber. Weight gain was recorded as a function of time. The sample was then placed into a small-scale reactor. The glove boxes used for loading and surveillance were flushed with He, resulting in a glove box atmosphere of mainly He with a small amount of air. Some moisture loss was expected during transfer from the humidified chamber into the SSR in the very dry glove box atmosphere (relative humidity < 0.1 %). Transfer time from the balance where the final mass measurement is made to when the SSR was sealed was kept to approximately 45 seconds. Weight loss during transfer for high-purity oxides was measured to be 0.07 wt% per minute.⁸ This correction was applied to obtain the estimated moisture content.

The sealed SSR was placed in a heated sample array maintained at 55 °C. Fifty microliter gas samples (~1.1 % of the headspace gas per sample) were extracted through a gas manifold and analyzed using an Agilent 5890 GC (gas chromatograph) calibrated for He, H₂, N₂, O₂, CO₂, CO and N₂O. Water vapor was not measured in these samples. The pressure and array temperature was recorded every fifteen minutes. The pressure data was reduced to weekly average values reported here. Gas composition was sampled at least annually.

At the termination of the experiment, a final GC gas sample was taken, and the SSR was removed from the array and allowed to cool to glove box temperature. The SSR lid was removed and a new lid containing a relative humidity sensor was placed on the container. After allowing for the system to equilibrate, the relative humidity and temperature in the container were measured using a Vaisala HMT330 sensor and readout. The material was then removed from the container and the moisture content in the material was determined by performing LOI-200 °C.

Results

Loading

A ten-gram split from the parent was selected for loading into each of the SSRs. The mass of the sample prior to moisture loading, m_{mat} , the volume the material occupies calculated from m_{mat} and the pycnometer density, V_{mat} , and the calculated free gas volume within the SSR, V_{gas} , during the gas generation study are given in Table 4. The pycnometer density of 8.3 g cm^{-3} , measured for the material in SSR129, was used for both reactors. The pycnometer density for the calcined material in SSR129A is expected to be higher, due to the 3-4% decrease in impurities compared with the material in SSR129. A higher density would result in a larger Free Gas Volume in the reactor.

Table 4. Mass of sample and results of calculation of free gas volume using approach in *Obtaining G-values and rate constants from MIS data* Appendix A.⁶

| SSR | Mass of sample m_{mat} | Volume of Material V_{mat} | Volume of SSR V_{SSR} | Free Gas Volume in SSR V_{gas} |
|------|------------------------------------|--|-----------------------------------|--|
| 129 | 10.01 g | 1.21 cm^3 | 5.326 cm^3 | 4.12 cm^3 |
| 129A | 10.01 g | 1.21 cm^3 | 5.326 cm^3 | 4.12 cm^3 |

TGA-MS Results

TGA-MS data for the material in SSR129 is shown in Figure 5. The sample was large enough to split into three subsamples. TGA traces for all three subsamples and MS traces for channels that were above background for one of the three samples are illustrated. Total moisture content was determined to be 0.87 wt%. During the TGA-MS analysis, 0.067 wt% carbon dioxide (mass 44), 0.089 wt% nitrogen dioxide (mass 46), and 2.7 wt% sulfur dioxide (mass 16, 32 and 64) was released. The LOI-200 °C loss of 0.45 wt% underestimates the amount of water for this material that includes 60% AR material. No TGA results are available for the material loaded in SSR129A.

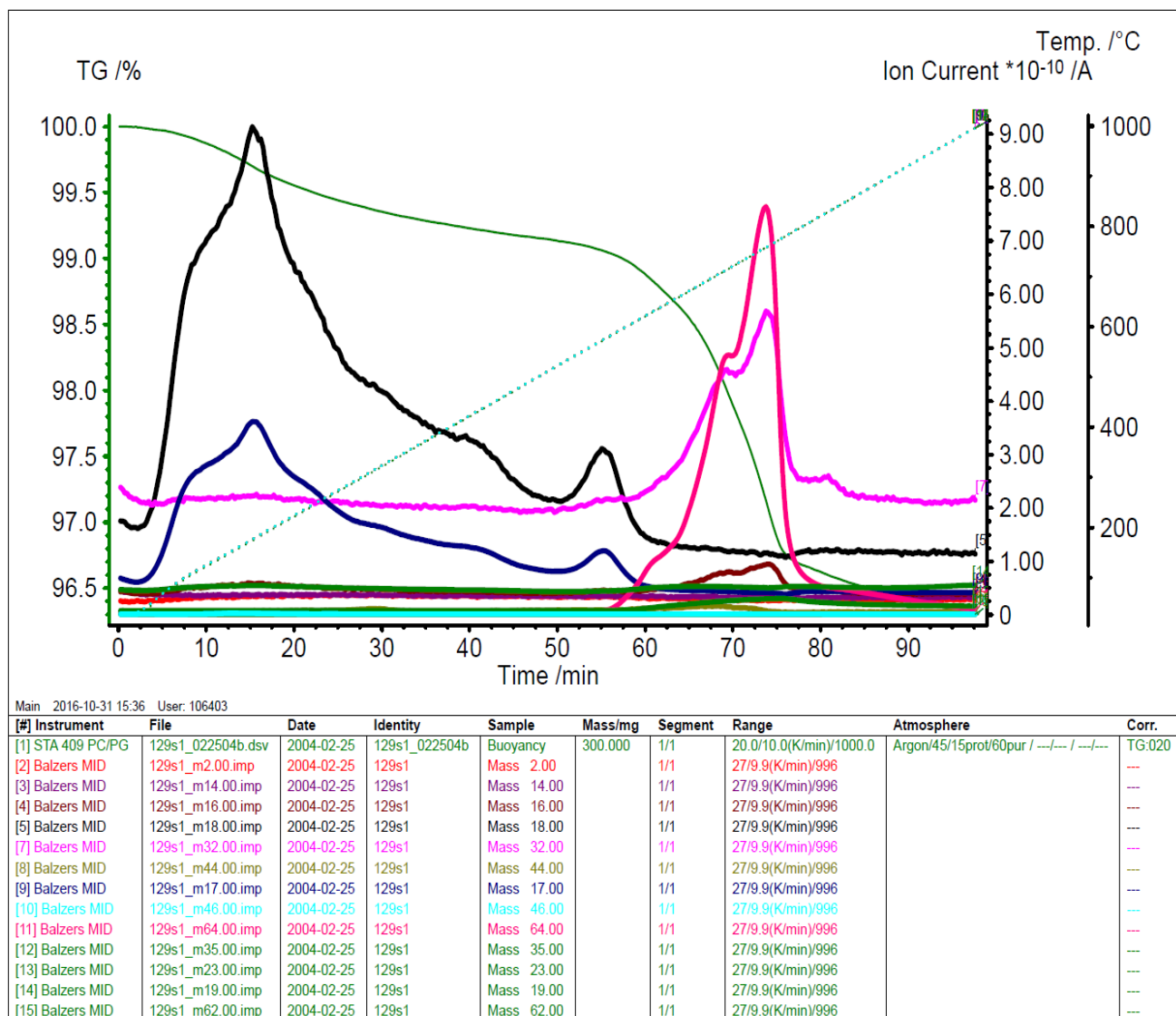


Figure 5. TGA-MS data for the material loaded in SSR129.

Moisture addition

The measurements and assumptions used to calculate the moisture content at the time of loading are summarized in Table 5. The best value for the moisture content at loading for SSR129 is 0.82 wt% as given in Table 5, line 12, Estimated Total Moisture in loaded sample (using TGA-MS). Because TGA-MS data is not available for SSR129A, the best value for moisture at loading for SSR129A is 0.35 wt% as given in Table 5, line 13, Estimated Total Moisture in the loaded sample (using LOI).

Table 5. Moisture data summary at loading.

| | Parameter | SSR129 | SSR129A | Units |
|----|---|-----------------------------------|---------------------------------------|-------|
| 1 | Most recent Calcination Date | AR (60%) July 7, 1997 (40%) | 7/30/97 (53%) 11/19/03 (47%) | |
| 2 | Loading Date | 01/07/04 | 10/24/05 | |
| 3 | Unloading Date | 06/27/2007 | 06/27/2007 | |
| 4 | Initial sample weight (m_{mat}) | 10.01 | 10.01 | g |
| 5 | Initial Moisture (Total) by TGA-MS | 0.87 | n/a | wt% |
| 6 | Initial Moisture (Weakly bound) by LOI-200 °C | 0.45 | 0.04 | wt% |
| 7 | Estimated additional (chemisorbed) moisture present = 1.5 ML | 0.10 | 0.02 | wt% |
| 8 | Total Moisture added | 0.0 | 0.34 | wt% |
| 9 | Relative Humidity in glove box during loading | 0.1 | 0.1 | % |
| 10 | Estimated moisture loss during loading | 0.05 | 0.05 | wt% |
| 11 | Estimated Weakly Bound Moisture in loaded sample (using LOI) = Line 6 +Line8 –Line 10 | 0.4 | 0.31 | wt% |
| 12 | Estimated Total Moisture in loaded sample (using TGA-MS) = Line 5 + Line 8 –Line 10 | 0.82 | n/a | wt% |
| 13 | Estimated Total Moisture in loaded sample (using LOI) = Line 6 +Line7 +Line 8–Line 10 | 0.50 | 0.35 | wt% |

No additional moisture was added to the material in SSR129 because total moisture was already above the desired 0.5 wt% target. The moisture uptake as a function of exposure time to a high humidity atmosphere for SSR129A is plotted in Figure 6. After 30 seconds a heater to the moisture bowl was turned on to increase the rate of moisture absorption. The water temperature increased to 41.3 °C and the chamber temperature increased to 37.4 °C by the end of the run. The rapid moisture gain observed is unexpected for a material with a SSA of 0.67 m²/g and little salt. This suggests that the material contains a component that adsorbs water. Some loss of water occurs when the material is transferred from the humidified chamber to the balance where the final mass measurement is made. Thus, the total moisture added in Table 5, line 8, 0.34 wt%, is 0.05 wt% less than the mass gain during moisture uptake, 0.39 wt%.

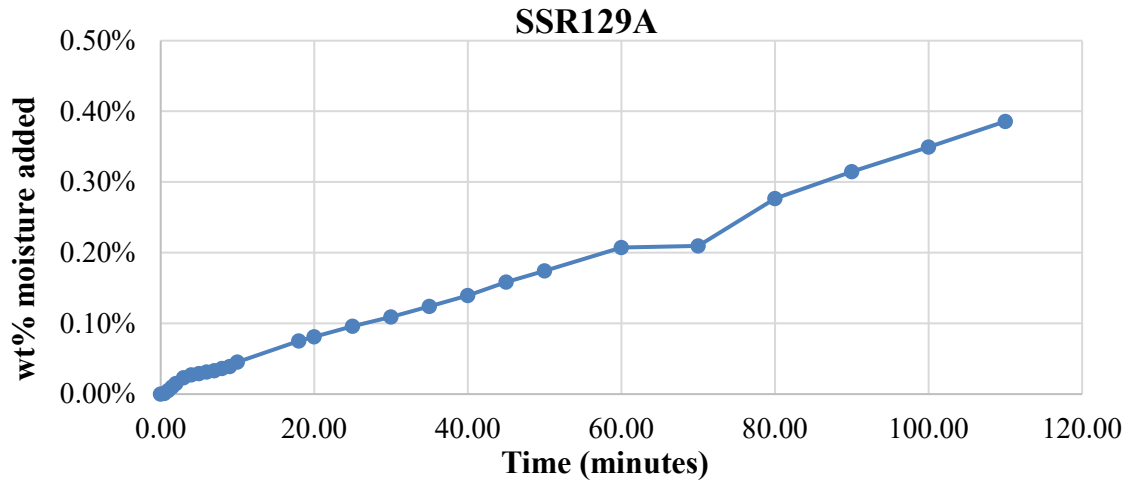


Figure 6. Moisture Addition Curve for SSR129A

Gas Generation

The total pressure in SSR129 and SSR129A as a function of time, as well as the partial pressure of several gases, are shown in Figure 7 and Figure 8. Detailed information on gas composition and uncertainties is in Attachment 1 and on total pressure in Attachment 2.

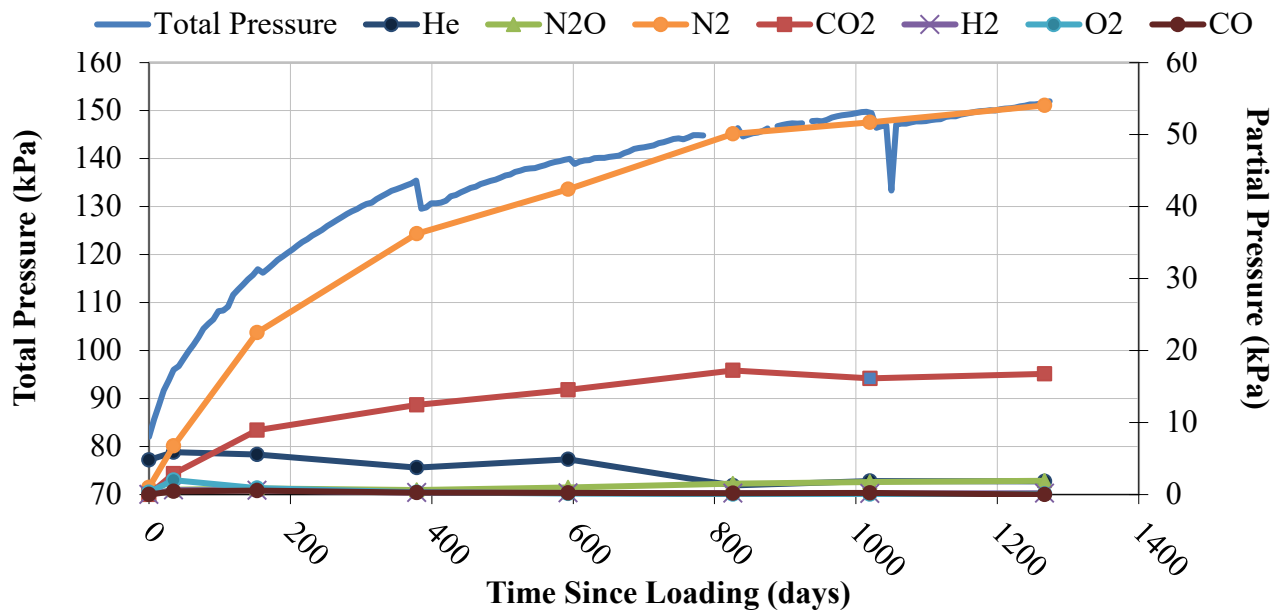


Figure 7. For SSR129, Total pressure (left axis) and partial pressure of gases (right axis) measured using a gas chromatograph as a function of time.

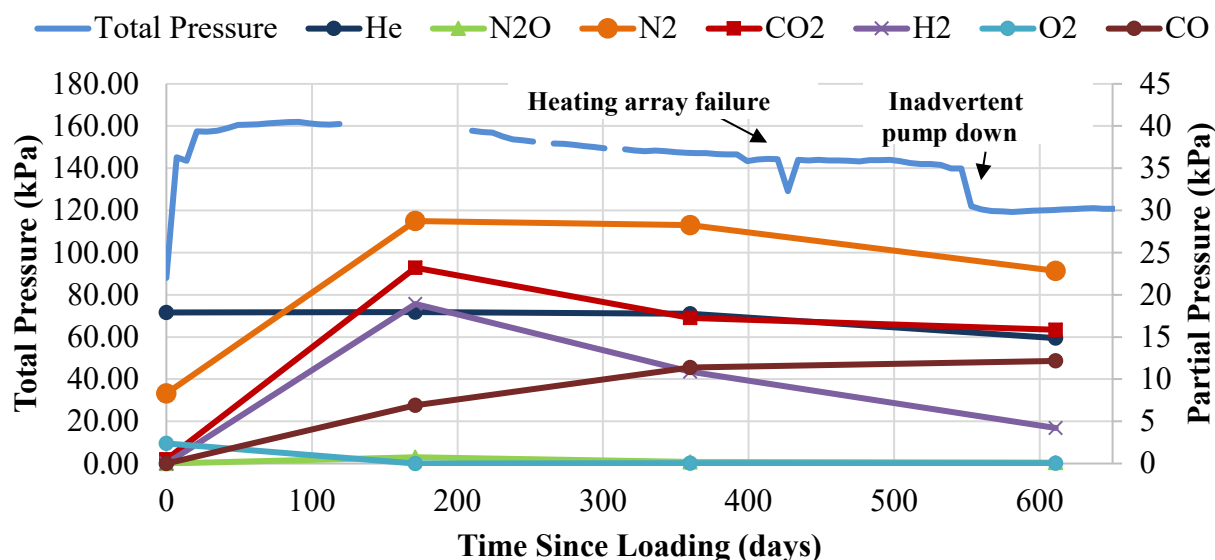


Figure 8. For SSR129A, total pressure and He partial pressure (left axis) and partial pressure of gases (right axis) measured using a gas chromatograph as a function of time.

In SSR129, the total pressure increased from an initial pressure of 82 kPa to a maximum of 152 kPa by 1274 days when the experiment was terminated. Nitrogen, which was the major contributor to the pressure rise, started with an initial pressure of 1.0 kPa that increased to 54.1 kPa by the end of the experiment. Carbon dioxide also started with a low initial pressure that increased to a maximum pressure of 17.2 kPa after 826 days. Hydrogen pressure increased slowly to a maximum of 0.6 kPa after 35 days before slowly decreasing. Oxygen behaved similarly, reaching a maximum of 2.0 kPa. Helium partial pressure decreased gradually from 77.2 kPa to a final pressure of 72.7 kPa, due to sampling. Little or no nitrous oxide, methane, and carbon monoxide were generated.

In SSR129A, total pressure increased rapidly in the first week from an initial pressure of 88 kPa to a pressure of 145 kPa, reaching a near maximum of 157 kPa in 21 days where it stayed for three months. This sudden pressure rise was probably due primarily to the release of N₂, CO₂ and CO from the surface, as well as hydrogen generation. This sudden pressure rise is unusual and unexplained but does not present a safety concern. The total pressure then trended downward until an inadvertent pump down in the reactor around 500 days resulted in a sudden drop in the total pressure. A power outage resulted in no data sampling between days 100 and 200. A heating array failure around 400 days resulted in a steep dip in the total pressure. Hydrogen partial pressure reached a maximum-recorded value of 18.9 kPa, then declined. Nitrogen, carbon dioxide, hydrogen and carbon monoxide all played significant roles in the sudden increase in initial overall pressure in SSR129A with partial pressures at 28.7 kPa, 23.2 kPa, 18.9 kPa, and 12.2 kPa, respectively. There was a slight drop in pressure in all of the gases except carbon monoxide at the next gas sampling. Oxygen partial pressure was initially 2.4 kPa, then dropped to less than 0.1 kPa. Due to the apparent inadvertent pump down of the reactor after 500 days, the fourth data points are lower than would have been expected.

Moisture measurements on unloading

The SSRs were removed from the heated array and placed in a holder to cool. The SSR lid was removed and a new lid containing a relative humidity sensor was placed on the container in 66 sec for SSR129 and 35 sec for SSR129A. After allowing the system to equilibrate, the relative humidity and temperature in the container were measured. The weight loss in the material at termination for SSR129A by performing LOI-200 °C was 0.02 wt%. A measurement was not obtained for SSR129. To estimate the total moisture at unloading, an additional 1.5 ML was added to estimate the chemically adsorbed water not removed by heating to 200 °C.

For SSR129A, the unloading LOI-200 °C (0.02 wt%) was 0.02 wt% less than the LOI-200 °C (0.04 wt%) at loading. Carbon and nitrogen surface species were lost to the gas phase as CO₂, CO, and N₂, and are quantified in the TGA discussion. Desorption of these gases from the sample could account for some of the difference between the initial and final LOI.

Given the measured RH at unloading of 0.1% at 29.1 °C (SSR129) and 21.4% at 26.7 °C (SSR129A), BET theory predicts that ~ 0.01 ML (0.0007 wt%) and 0.83 ML (0.012 wt%), respectively, physisorbed water was present in the reactors. Assuming an additional 1.5 ML (0.1 wt% and 0.02 wt% respectively) present as chemisorbed water, the RH estimates of the moisture on the material at unloading are 0.10 wt% in SSR129 and 0.034 wt% in SSR129A. (See Appendix 3.)

Sample unloading and moisture data are summarized in Table 6.

Table 6. Unloading moisture data summary

| | Parameter | SSR129 | SSR129A | Units |
|---|---|----------|-----------|-------|
| 1 | Unloading Moisture by LOI-200 °C | N/A | 0.02 | wt% |
| 2 | Estimated additional (chemisorbed) moisture present = 1.5 ML | 0.10 | 0.022 | wt% |
| 3 | Estimated total moisture at unloading by LOI = Line 1 + Line 2 | N/A | 0.04 | wt% |
| 4 | Relative Humidity/Temperature in headspace at unloading | 0.1/29.1 | 21.4/26.7 | %/ °C |
| 5 | Number of monolayers at unloading RH and temperature using Figure A-1 or Eq. A- and c=7 | 0.01 | 0.83 | ML |
| 6 | Mass of weakly bound water (RH) using # of MLs in line 5. | 0.0007 | 0.012 | wt% |
| 7 | Estimated total moisture at unloading from RH and temperature = line 2 + line 6 | 0.1007 | 0.034 | wt% |

Corrosion

Figure 8 and Figure 9 show images of the inner buckets used for SSR129 and SSR129A.

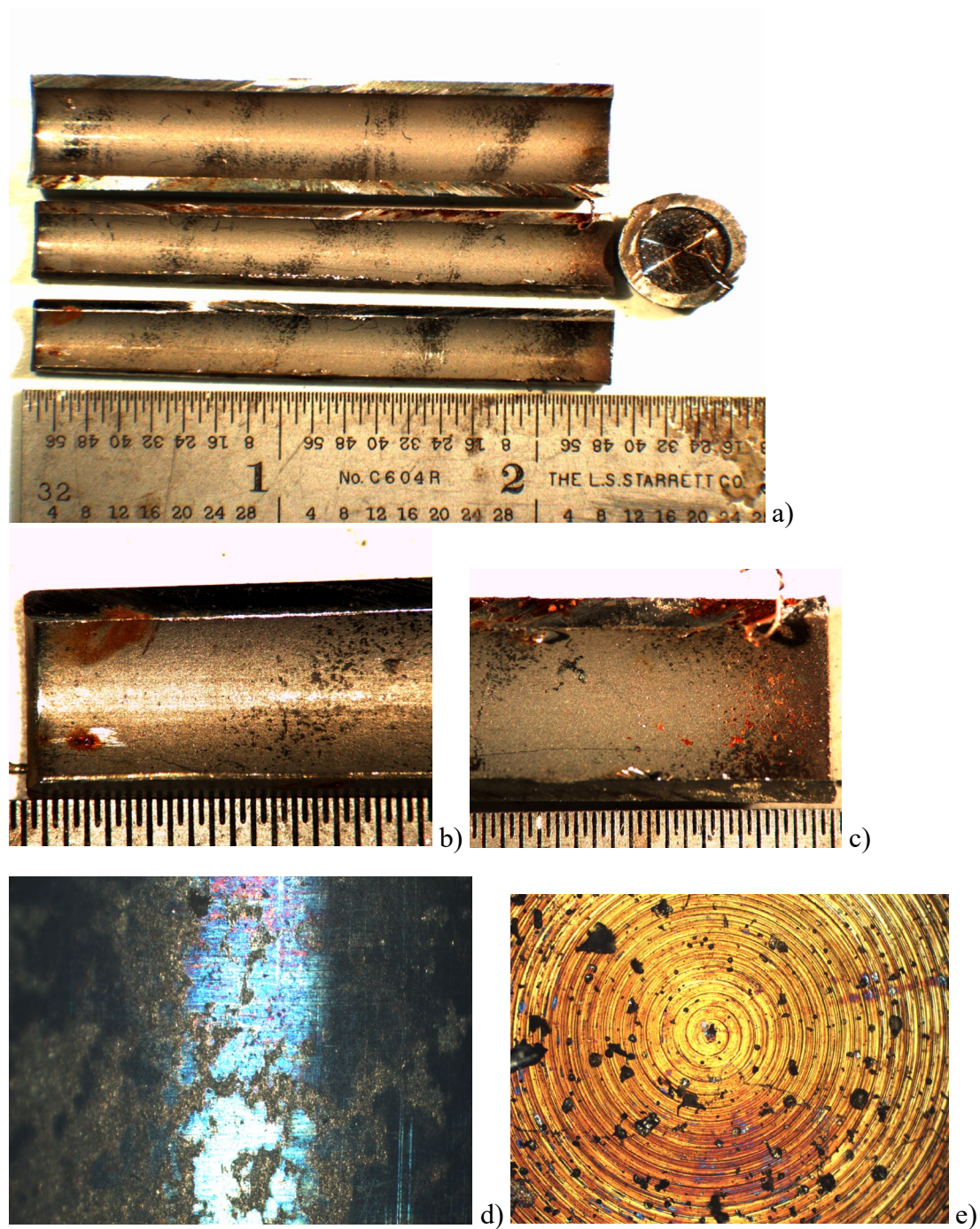


Figure 8. Photographs after unloading SSR129: a) inner bucket b) & c) Macrographs of inner wall showing red material, possibly corrosion product d) suspect corrosion of inner wall and e) suspect corrosion of bottom of the inner bucket (black regions appear to be material on surface)

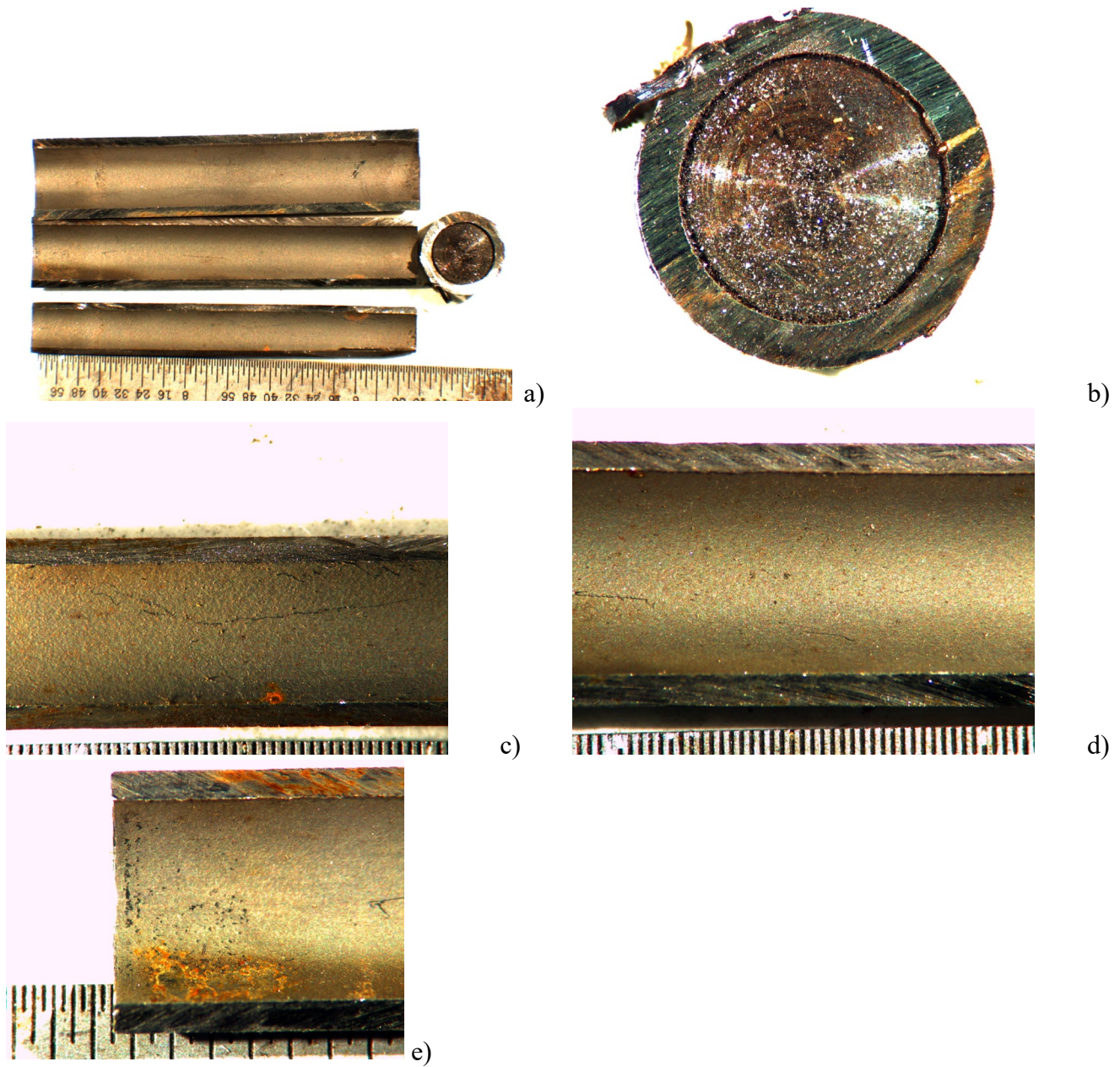


Figure 9. Photographs after unloading SSR129A: a) inner bucket b) suspect corrosion of bottom of inner bucket c), d), & e) suspect corrosion on inner walls of bucket.

Suspect corrosion was observed within SSR129 and SSR129A. A rust colored coating was observed on the inner walls of the buckets for both containers.

Discussion

A goal of the small-scale surveillance studies is to understand the hydrogen gas generation response of material exposed to moisture over a broad range of materials. Recommendations on the analysis of hydrogen partial pressure curves include calculations to obtain hydrogen G-values and formation and consumption rate constants assuming that the hydrogen gas is formed either from radiolysis or from surface reactions with water.⁶ In order to perform these calculations, knowledge of the moisture content of the material during the study and the dose to the moisture is required. We will first discuss the amount of moisture on the material during the study and use the results as input to the $G(H_2)$ and rate constant calculations. We will follow those results with a discussion of the observation of other gases.

Unlike plutonium-bearing materials currently stored in 3013 containers throughout the DOE complex, the material in reactors SSR129 and SSR129A contained material that was either not calcined after arrival or was exposed to air for two to eight years after calcination prior to loading. A significant formation of hydroxyls on the oxide surface is expected after this much time. Gases, such as CO_2 or NO_x , would also be adsorbed to the surface and come off of the material when moisture is added to the system. The presence of these species may alter the gas generation behavior compared with recently calcined (to 950 °C) plutonium/uranium oxide.

The amount of hydrogen generated as well as the RH at unloading provides additional insight into whether uranium is present as U_3O_8 or a hydrated UO_3 compound. Studies of water associated with U_3O_8 and UO_3 exposed to gamma radiation show that water associated with UO_3 generates H_2 at ten times the rate of water associated with U_3O_8 , but less than water that is ten monolayers thick on an oxide surface.^{4a, 9} Generation of a small amount of H_2 ($P_{max} = 0.6$ kPa) and, in particular, the very low RH at unloading in SSR129 (0.1%), suggests a hydrated UO_3 was present in the oxide that contained 60% AR material. This behavior is very similar to that observed in SSR135.¹⁰ When U_3O_8 is stored under high RH conditions near 90%, $UO_3 \cdot 2.25H_2O$ and $UO_3 \cdot 2H_2O$ are formed within 3.5 years.^{4b} Part of the calcined material was stored in the vault at a lower RH, probably near 30% (ranged from 17 -34%, depending on the room). It would be reasonable that the material after years in the vault contained a small amount of hydrated UO_3 .

The H_2 G-value

Figure 10 illustrates the significantly lower hydrogen generation in SSR129 compared with SSR129A as a function of time.

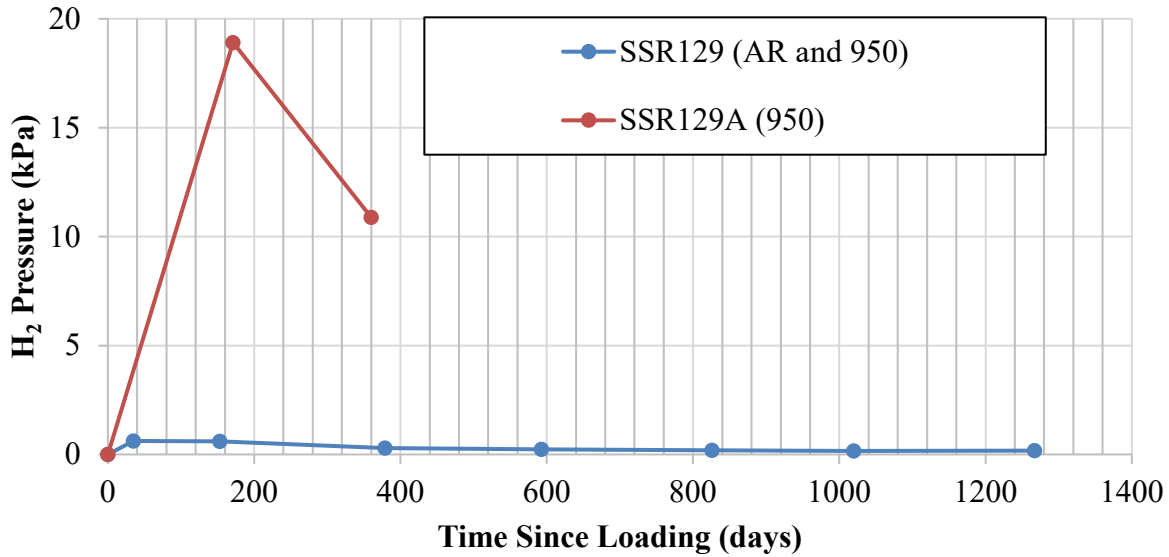


Figure 10. Hydrogen Pressure as a function of time in SSR129 and SSR129A

For SSR129, the H₂ partial pressure increased by 0.6 kPa during the first 60 days, indicating a lower limit for the initial production rate of 0.01 kPa/day. For SSR129A, the H₂ partial pressure increased by 18.9 kPa in the first 171 days, indicating a lower limit for the initial production rate of 0.11 kPa/day. Because of the long delay before hydrogen concentration was measured, a more accurate estimate of the initial hydrogen generation rate in SSR129A can be determined by looking at total pressure. A pressure rise of 57 kPa was measured in the first 7 days (which accounted for 80% of the total pressure rise in the reactor per Appendix 2). GC results in Appendix 1 indicate that 27% of this rise is attributed to hydrogen. This translates to an estimated initial hydrogen production rate of 2.2 kPa/day = 57 kPa/7day * 0.27.

For SSR129, the H₂ pressure at long times approached a non-zero value, suggesting a back reaction that reformed H₂ was occurring. The formation and consumption of H₂ can be represented in a simple scheme as:



The H₂ pressure is given by assuming P_{H_2} is zero at $t=0$,

$$P_{H_2}(t) = A_0 \left(1 - e^{-k_1 t} - \frac{k_2}{k_2 + k_3} \left(1 + \frac{k_1}{k_2 + k_3 - k_1} e^{-(k_2 + k_3)t} - \frac{k_2 + k_3}{k_2 + k_3 - k_1} e^{-k_1 t} \right) \right) \quad \text{Equation 2}$$

where A_0 is the amount of water expressed in units of pressure in the reactor involved in hydrogen generation at $t=0$, t is time in days, and k_1 , k_2 and k_3 are the first-order rate constants for the formation, consumption and the back reformation of hydrogen in days⁻¹.

The initial rate is

$$\text{Initial rate} = A_0 k_1. \quad \text{Equation 3}$$

The time of the maximum pressure is given by

$$t_{max} = \frac{\ln\left(\frac{k_2}{k_1 - k_3}\right)}{k_2 + k_3 - k_1} \quad \text{Equation 4}$$

The maximum pressure is given by

$$P_{max} = \frac{A_0}{(k_2 + k_3)(-k_2 - k_3 + k_1)} \left[k_2 k_3 + k_3^2 - k_1 k_3 - k_2 k_3 \left(\frac{k_1 - k_3}{k_2} \right)^{-\frac{k_1}{-k_2 - k_3 + k_1}} + k_1 k_2 \left(\frac{k_1 - k_3}{k_2} \right)^{-\frac{k_1}{-k_2 - k_3 + k_1}} - k_3^2 \left(\frac{k_1 - k_3}{k_2} \right)^{-\frac{k_1}{-k_2 - k_3 + k_1}} + k_1 k_3 \left(\frac{k_1 - k_3}{k_2} \right)^{-\frac{k_1}{-k_2 - k_3 + k_1}} - k_1 k_2 \left(\frac{k_1 - k_3}{k_2} \right)^{-\frac{k_2 + k_3}{-k_2 - k_3 + k_1}} \right] \quad \text{Equation 5}$$

and the H₂ pressure at long times is given by

$$P_{H_2}(t \rightarrow \infty) = \frac{k_3}{k_2 + k_3}. \quad \text{Equation 6}$$

The hydrogen partial pressure versus time observations for SSR129, fit to Equation 2, are shown in Figure 11. (Due to the inadvertent reactor pumpdown and limited number of data points, data from SSR129A was not fit.)

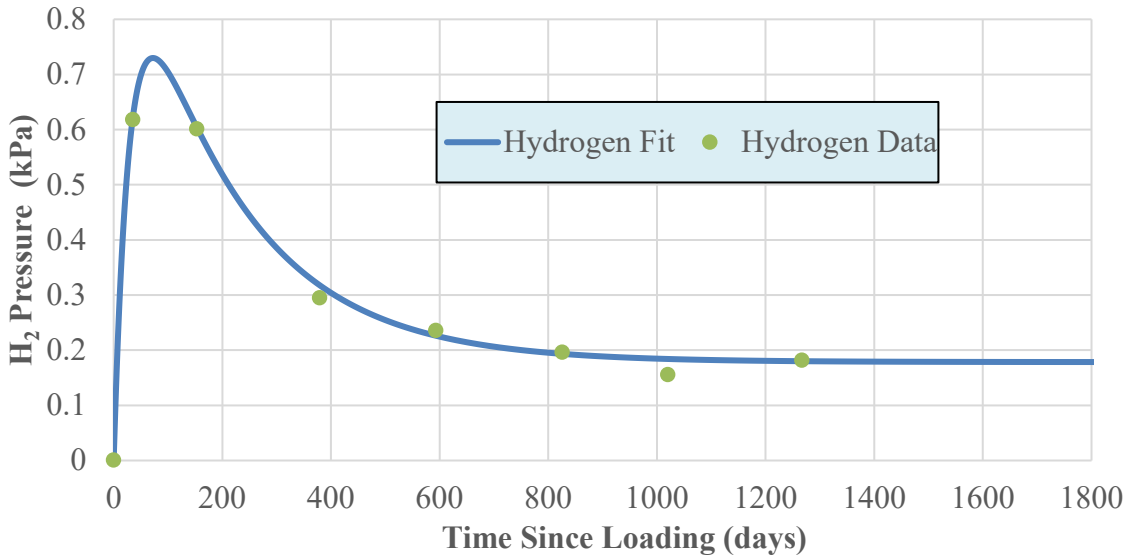


Figure 11. The hydrogen partial pressure and the fit to Equation 2, or first order formation, first order consumption reaction and first order formation back reaction for SSR129.

The values for the fit parameters yielding the curves in Figure 11, along with the standard error in the parameters, are given in Table 7. The function reached a maximum of 0.73 kPa at 71 days. The initial rate of hydrogen generation calculated from these parameters was 0.033 kPa/day.

Table 7. The fit parameters, standard errors and initial rate from the hydrogen generation data for SSR129 at 55 °C from the fit to Equation 2.

| Small-scale Surveillance sample ID | A_0 <i>kPa</i> | k_1 (day ⁻¹) | k_2 (day ⁻¹) | k_3 (day ⁻¹) | Initial Rate (<i>kPa/day</i>) ($k_1 A_0$) |
|------------------------------------|---------------------|-------------------------------|-------------------------------|-------------------------------|---|
| SSR129 | 6.6 | 0.0050 | 0.033 | 0.00092 | 0.033 |
| Standard Error | 1.1 | 0.0006 | 0.004 | 0.00012 | |

The low initial water involved in hydrogen generation, A_0 , determined from the fit, corresponds to 0.0018 wt% or approximately 0.2% of the estimated total moisture in the loaded sample (Table 5, line 12). This suggests that the majority of the water was present as a hydrate ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) and was not involved in hydrogen generation. The estimated wt% water involved in hydrogen formation (A) remaining in the system as a function of time is plotted in Figure 12 using the Equation 7 below.

$$A(t) = A_0 e^{-k_1 t} \quad \text{Equation 7}$$

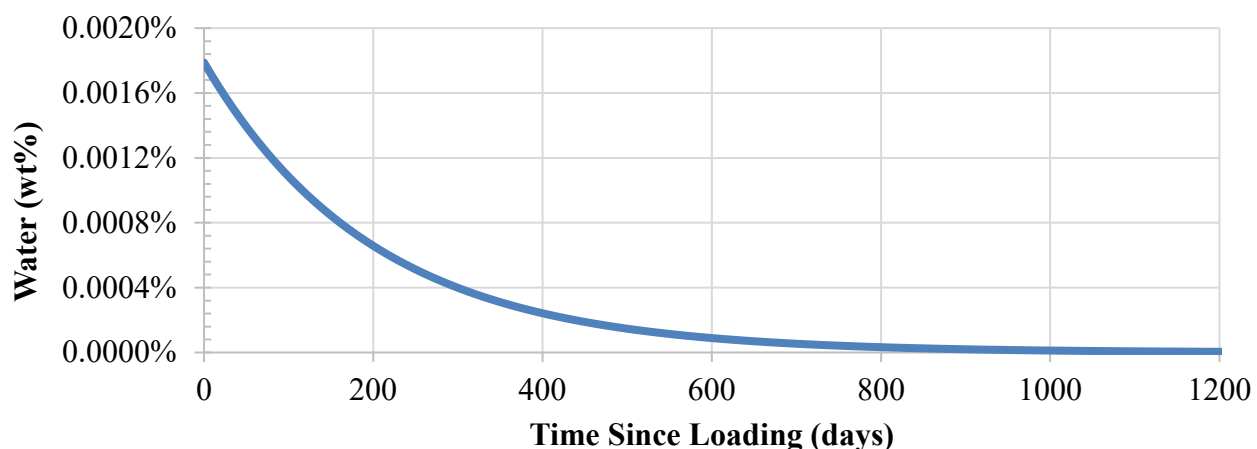


Figure 12. Graph of the estimated water involved in hydrogen generation $A(t)$ in SSR129 as a function of time, where A_0 is expressed in terms of wt% of water (Equation 7). The plot indicates that all of the initial water involved in hydrogen generation reacted to form hydrogen by the termination of the experiment.

Estimation of the amount of moisture on the material during the gas generation study

Results suggest that the 5501579 material in SSR129, which was a mixture of AR and calcined to 950 °C, contains PuO_2 and U_3O_8 with a small amount of UO_3 . UO_3 picks up water and forms hydrates such as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ when exposed to moisture.⁴ Moisture adsorption by high-purity PuO_2 and U_3O_8 is very small^{4a} and the moisture is thought to exist as physisorbed water that behaves according to BET theory¹¹ and as chemically bound water with very low chemical activity (very low water vapor pressure). The latter water can be described as surface hydroxyls and is removed from the oxide surfaces only at high temperatures. The best estimate of the moisture at loading for SSR129 is 0.82

wt%. A monolayer of moisture is 0.07 wt%, thus the amount of moisture at loading if it is all physically and chemically adsorbed onto the $3.18 \text{ m}^2 \text{ g}^{-1}$ surface represents approximately 11.7 monolayers. If UO_3 were present, formation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is likely. The water would then be partitioned as follows. At loading, 1.5 monolayers (0.10 wt%) as hydroxyls, 0.01 monolayers physisorbed from BET using RH at unloading (0.0007 wt%), with the remainder as hydrates associated with UO_3 (0.72 wt%). At unloading, 1.5 monolayers as hydroxyls (0.10 wt%), 0.01 monolayers as physisorbed at a RH of 0.1 % (0.00007 wt%), the equivalent of 0.6 kPa dissociated as H_2 (0.0002 wt%), water vapor at 0.1% RH at 29°C (1×10^{-6} wt%), and the remainder still associated with UO_3 as hydrates (0.72 wt%). In previous small scale reactor studies, water condensed in colder regions of system piping. However, the very low RH at unload would not have been observed if condensed water were present. Table 8 summarizes the amount of water on the material, in the gas phase, and decomposed to form H_2 expressed as weight percent, moles, grams, and monolayers.

Table 8. The amount of water adsorbed on the material in SSR129, in the gas phase, and decomposed to form H_2 expressed as moles, grams, and monolayers. The mass of water in a monolayer is 0.007 g. Calculations use $\text{SSA} = 3.18 \text{ m}^2 \text{ g}^{-1}$, $m_{\text{mat}} = 10.01 \text{ g}$ and $V_{\text{gas}} = 4.1 \text{ cm}^3$. The amount of chemisorbed water on the material was assumed to be 1.5 ML at all times.

| Water Source | Amount of Water | | | |
|---|------------------------------------|----------------------|----------------------|------------------------------------|
| | wt% | g | Moles | monolayers |
| | 0.070 | 0.0070 | 3.9×10^{-4} | 1 |
| Estimated total moisture in loaded sample from Table 5 | 0.82 | 0.082 | 0.0046 | 11.7 |
| Water as hydroxyls | 0.10 | 0.01 | 5.9×10^{-4} | 1.5 |
| Water consumed to form H_2 ($P_{\text{max}} = 0.60 \text{ kPa}$) | 0.00016 | 1.6×10^{-5} | 9×10^{-7} | 0.0023 |
| Water from fit ($A_0 = 6.6 \text{ kPa}$) | 0.0018 | 1.8×10^{-4} | 1.0×10^{-5} | 0.026 |
| On material at unloading from BET using RH and $c = 7$ | 0.0007 | 7.0×10^{-5} | 3.9×10^{-6} | 0.01 |
| Water vapor at unloading, 29.1°C and 0.1% RH (0.004 kPa) | 1×10^{-6} (equivalent) | 1×10^{-7} | 6×10^{-9} | 2×10^{-5} (equivalent) |
| On material at unloading by LOI | Not measured | | | |
| Presumed present as hydrates at unloading = Estimated total moisture in the loaded sample from Table 5 - water consumed -water vapor at unload - hydroxyls - physisorbed from RH | 0.72 | 0.072 | 0.004 | 10.2 |

(Note: Additional moisture could have been consumed in formation of the corrosion products such as iron hydroxide)

The 5501579 material in SSR129A calcined to 950 °C contains PuO₂ and U₃O₈ with perhaps a small amount of UO₃. The best estimate of the moisture at loading for SSR129A is 0.35 wt% (Table 5). A monolayer of moisture is 0.015 wt%, thus the amount of moisture at loading if it is all physically and chemically adsorbed onto the 0.67 m² g⁻¹ surface represents approximately 23.3 monolayers. The relatively high hydrogen generation and in particular, the RH at unloading (21.4%), suggest that there was not a significant amount of water present as hydrates (UO₃·2H₂O). Instead, the loosely bound physisorbed water condensed in colder regions of the piping. This condensation has been postulated in previous reports.¹² Table 9 summarizes the amount of water on the material, in the gas phase, and decomposed to form H₂ expressed as weight percent, moles, grams, and monolayers.

Table 9. The amount of water adsorbed on the material in SSR129A, in the gas phase, and decomposed to form H₂ expressed as moles, grams, and monolayers. The mass of water in a monolayer is 0.007 g. Calculations use SSA = 0.67 m² g⁻¹, m_{mat} = 10.01 g and V_{gas} = 4.1 cm³. The amount of chemisorbed water on the material was assumed to be 1.5 ML at all times.

| Water Source | Amount of Water | | | |
|---|---------------------|----------------------|------------------------|-------------------|
| | wt% | g | Moles | monolayers |
| | 0.015 | 0.0015 | 8 x 10 ⁻⁵ | 1 |
| Estimated total moisture in loaded sample from Table 5 | 0.35 | 0.035 | 0.0019 | 23.3 |
| Water as hydroxyls | 0.022 | 0.0022 | 1.2 x 10 ⁻⁴ | 1.5 |
| On material at unloading from BET using RH and c = 7 | 0.012 | 0.0012 | 7 x 10 ⁻⁵ | 0.83 |
| Water consumed to form H ₂ (18.9 kPa) | 0.005 | 0.0005 | 3 x 10 ⁻⁵ | 0.07 |
| Water vapor at unloading, 26.7 °C and 21.4% RH (0.75 kPa) | 0.0002 (equivalent) | 2 x 10 ⁻⁵ | 1 x 10 ⁻⁶ | 0.01 (equivalent) |
| On material at unloading by LOI | 0.02 | 0.002 | 1.1 x 10 ⁻⁴ | 1.4 |
| Estimated total moisture from unloading data = water consumed + water vapor + hydroxyls + LOI | 0.047 | 0.0047 | 2.6 x 10 ⁻⁴ | 3.3 |
| Presumed condensed in piping = Estimated total moisture in loaded sample from Table 5 – Estimated total moisture in loaded sample from unloading data | 0.30 | 0.030 | 0.0017 | 20 |

(Note: Additional moisture could have been consumed in formation of the corrosion products such as iron hydroxide)

For SSR129, A_0 and k_1 are used to calculate $G(H_2)$ for the hydrogen, using equation A5-4 in Appendix 5. Because of the uncertainty in determining the amount of water involved in the hydrogen generation, several values are used for the variable m_{H_2O} for comparison. The stopping power ratio for 5501579 material in SSR129, $\frac{S_{H_2O}}{S_{mat}}$, is 3.57 (Appendix 4). Results for the multiple choices of water, using equations from Appendix 5, are reported in Table 10. $G(H_2)$ for SSR129A calculated using an initial rate of 2.2 kPa/day (A_0k_1) and two estimated moisture contents are also reported in Table 10.

Table 10. $G(H_2)$ for SSR129 and SSR129A calculated from estimated moisture content using equation A5-4 in Appendix 5 assuming radiolytic decomposition of water to form H_2 .

| SSR129 | | | |
|---|------------|--------|------------------------|
| Variable | m_{H_2O} | Value | Units |
| $G(H_2)$ from estimated total moisture in loaded sample from Table 5 | 0.082 g | 0.012* | molecules $100eV^{-1}$ |
| $G(H_2)$ from A_0 from fit | 0.00018 g | 5.3 | molecules $100eV^{-1}$ |
| $G(H_2)$ from H_2 max pressure | 0.000016 g | 47.6 | molecules $100eV^{-1}$ |
| $G(H_2)$ from RH at unloading | 0.00007 g | 13.5 | molecules $100eV^{-1}$ |
| SSR129A | | | |
| $G(H_2)$ from estimated total moisture in loaded sample from Table 5 | 0.035 g | 1.8 | molecules $100eV^{-1}$ |
| $G(H_2)$ from estimated total moisture from unloading data from Table 9 | 0.0047 g | 14 | molecules $100eV^{-1}$ |

*Icenhour et. al reported a $G(H_2)$ value 0.01 molecules $100eV^{-1}$ for gamma radiolysis of $UO_3 \cdot 2H_2O$ ^{4a}

For SSR129A, while the two values bound the possible moisture on the material that contributes to radiolysis, we consider 0.035g, the mass resulting in 1.8 molecules $100eV^{-1}$, to be more likely because (1) the water uptake is rapid indicating the presence of a species that holds the water on the material and (2) the RH at unloading of 21% is too low for significant condensation in the piping. Figure 13. compares key $G(H_2)$ values determined in this study with those reported previously.⁹

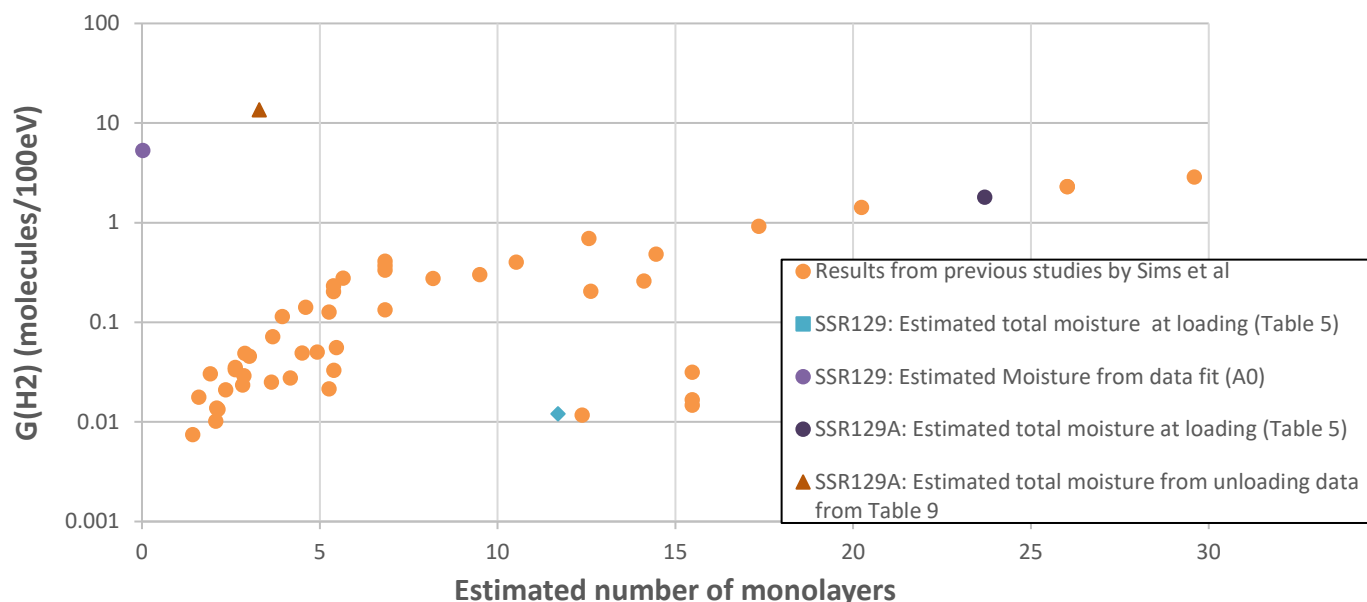


Figure 13. Comparison of select calculated $G(H_2)$ for SSR129 and SSR129A plotted against the number of calculated water monolayers determined in this study with those from previous research.

Behavior of CO_2 and NO_2

The CO_2 and NO_2 detected by TGA-MS on the 10 g sample at loading are possible sources for the CO_2 , CO, N_2O and N_2 observed in the gas phase. (The compounds actually bound to plutonium dioxide surface could have been any of the general forms CO_x and NO_x). The number of moles of CO_2 , CO, N_2O and N_2 present in the head space at the termination of the experiment were calculated using the ideal gas law, $n = PV/RT$, where $V = 4.1 \text{ cm}^3$, $T = 328 \text{ K}$, and P = partial pressure of the gas given in Attachment 1. Results are summarized in Table 11.

Table 11. Amount of carbon and nitrogen species detected on the surface prior to loading compared to the amount detected in the gas phase for SSR129.

| | CO_2 (moles) | CO (moles) | NO_2 (moles) | N_2O (moles) | N_2 (moles) | N (moles) |
|--|------------------------------------|-----------------------------------|----------------------|-----------------------------------|------------------------------------|----------------------|
| Sample (Loading- TGA-MS) | 1.5×10^{-4} | Not measured | 1.9×10^{-4} | Not measured | Not measured | 1.9×10^{-4} |
| Max Detected in Head Space over duration of experiment (GC) | 2.6×10^{-5} (17.2 kPa) | 9.1×10^{-7} (0.6 kPa) | Not measured | 2.9×10^{-6} (1.9 kPa) | 8.2×10^{-5} (54.1 kPa) | 1.7×10^{-4} |

In SSR129, approximately 20% of the carbon dioxide detected by TGA-MS was released from the surface primarily as CO_2 , and approximately 90% of the nitrogen was released from the

surface primarily as N₂. Prior to loading the sample in the small-scale reactor, the plutonium dioxide powder was exposed to air for years (nitrogen and oxygen with small amounts of water and carbon dioxide). The sample was placed in a helium atmosphere within the small-scale reactor with a large partial pressure of water. A possible explanation for the CO₂ observed in the headspace is that the water displaced chemically adsorbed CO₂ from the surface sites. The production of N₂ from the NO_x species adsorbed on the surface suggests that the reaction to form NO_x from radiolysis of air is reversible in the alpha radiation environment on the surface.

TGA-MS data was not available for the material in SSR129A.

Behavior of He

Alpha decay of the Pu and Am creates He, which may escape the oxide into the gas phase. The amount of He created depends upon the mass of the material and the rate of decay of the various isotopes. The rate of decay can be illustrated graphically as the specific wattage calculated from the reported isotopics, Figure 2. Results were calculated for SSR129 using the last reported isotopics measurements taken on December 1, 2003, which are reported in Table 3. The integrated and differential amount of He evolved as a function of time are shown in Figure 3.

The amount of He created due to alpha decay over the time the material was in the SSR is estimated to be 3.6×10^{-6} moles for the 10 g sample. This amount of He would result in a gas pressure increase of 2.4 kPa in the 4.1 ml of gas volume and gas temperature of 328 K, if all the He was released into the gas phase. A 6.4 kPa decline in He pressure is expected due to the eight gas samplings. He pressure declined by approximately 4.5 kPa, indicating 1.9 kPa, or 80% of the He was released into the gas phase. This analysis does not account for any leaks in the system or the large uncertainties associated with the He gas measurements.

Conclusions

A mixture of MIS item 5501579 containing 60% AR and 40% calcined to 950 °C material was entered into surveillance in January of 2004 and removed from surveillance in June of 2007. The amount of water on the material during the gas generation study was estimated to be 0.82 wt%. The gas generation was dominated by N₂ and CO₂. Hydrogen was generated to a maximum partial pressure of 0.6 kPa. The oxygen that was initially present (2.1 kPa) was mainly consumed.

A sample of MIS item 5501579 that had been calcined to 950 °C material was entered into surveillance in October of 2005 and removed from surveillance in June of 2007 when an inadvertant container pumpdown was detected. The amount of water on the material during the gas generation study was estimated to be 0.35 wt%. The gas generation was dominated by N₂, H₂, CO₂ and CO. The maximum measured partial pressure of hydrogen was 18.9 kPa. The oxygen that was initially present (2.4 kPa) was consumed.

In both reactors, suspect corrosion was observed on the walls and bottoms of the inner buckets.

Acknowledgements

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Appendix 1: Gas Generation Partial Pressure Data and Uncertainties in kPa

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Note: Total pressure values used to determine partial pressures were reduced by 4kPa to correct for the estimated partial pressure of water vapor. Partial pressures were corrected for variation in the sensitivity of the GC with time. The average manifold background pressure was subtracted from the partial pressures.

SSR129

| Date | 1/7/2004 | 2/11/2004 | 6/8/2004 | 1/20/2005 | 8/22/2005 | 4/12/2006 | 10/23/2006 | 6/27/2007 |
|------------------------------------|----------|-----------|----------|-----------|-----------|-----------|------------|-----------|
| Days | 0 | 35 | 153 | 379 | 593 | 826 | 1020 | 1267 |
| CO ₂ | 0.0 | 2.9 | 9.0 | 12.5 | 14.5 | 17.2 | 16.1 | 16.8 |
| N ₂ O | 0.0 | 0.7 | 0.8 | 0.6 | 1.0 | 1.5 | 1.7 | 1.9 |
| He | 77.2 | 78.8 | 78.3 | 75.6 | 77.3 | 71.9 | 72.8 | 72.7 |
| H ₂ | 0.001 | 0.62 | 0.60 | 0.30 | 0.24 | 0.20 | 0.16 | 0.18 |
| O ₂ | 0.3 | 2.0 | 0.9 | 0.3 | 0.1 | 0.1 | 0.1 | 0.1 |
| N ₂ | 1.0 | 6.7 | 22.5 | 36.2 | 42.4 | 50.1 | 51.7 | 54.1 |
| CH ₄ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| CO | 0.0 | 0.4 | 0.6 | 0.3 | 0.2 | 0.2 | 0.2 | 0.0 |
| Total Pressure – 4 kPa (Sum Check) | 78.6 | 92.2 | 112.7 | 125.9 | 135.9 | 141.2 | 142.8 | 145.7 |

Appendix 1: Gas Generation Partial Pressure Data and Uncertainties in kPa

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Uncertainties

| Date | 1/7/2004 | 2/11/2004 | 6/8/2004 | 1/20/2005 | 8/22/2005 | 4/12/2006 | 10/23/2006 | 6/27/2007 |
|------------------|----------|-----------|----------|-----------|-----------|-----------|------------|-----------|
| Days | 30 | 65 | 183 | 409 | 623 | 856 | 1050 | 1297 |
| CO ₂ | 0.00 | 0.09 | 0.22 | 0.29 | 0.34 | 0.39 | 0.37 | 0.38 |
| N ₂ O | 0.00 | 0.03 | 0.04 | 0.03 | 0.04 | 0.05 | 0.06 | 0.06 |
| He | 1.59 | 1.62 | 1.61 | 1.55 | 1.59 | 1.48 | 1.50 | 1.49 |
| H ₂ | 0.00 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| O ₂ | 0.02 | 0.06 | 0.04 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| N ₂ | 0.04 | 0.17 | 0.49 | 0.77 | 0.89 | 1.05 | 1.08 | 1.13 |
| CH ₄ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CO | 0.00 | 0.03 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.00 |

SSR129A

| Date | 10/24/2005 | 4/13/2006 | 10/19/2006 | 6/27/2007 |
|------------------------------------|------------|-----------|------------|-----------|
| Days | 0 | 171 | 360 | 611 |
| CO ₂ | 0.5 | 23.2 | 17.3 | 15.9 |
| N ₂ O | 0.0 | 3.0 | 0.7 | 0.4 |
| He | 71.6 | 71.8 | 71.0 | 59.5 |
| H ₂ | 0.0 | 18.9 | 10.9 | 4.2 |
| O ₂ | 2.4 | 0.0 | 0.0 | 0.0 |
| N ₂ | 8.3 | 28.7 | 28.3 | 22.8 |
| CH ₄ | 0.0 | 0.1 | 0.0 | 0.0 |
| CO | 0.0 | 6.9 | 11.4 | 12.2 |
| Total Pressure – 4 kPa (Sum Check) | 82.8 | 152.6 | 139.5 | 114.9 |

Appendix 1: Gas Generation Partial Pressure Data and Uncertainties in kPa

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Uncertainties

| Date | 10/24/2005 | 4/13/2006 | 10/19/2006 | 6/27/2007 |
|---------------------------------------|------------|-----------|------------|-----------|
| Days | 0 | 171 | 360 | 611 |
| CO ₂ | 0.03 | 0.51 | 0.39 | 0.36 |
| N ₂ O | 0.01 | 0.08 | 0.03 | 0.02 |
| He | 1.48 | 1.48 | 1.46 | 1.23 |
| H ₂ | 0.00 | 0.39 | 0.23 | 0.09 |
| O ₂ | 0.07 | 0.00 | 0.00 | 0.01 |
| N ₂ | 0.20 | 0.61 | 0.60 | 0.50 |
| CH ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| CO | 0.00 | 0.17 | 0.26 | 0.28 |
| Total Pressure – 4 kPa (Sum Check) | 82.8 | 152.6 | 139.5 | 114.9 |

Appendix 2: Gas Generation - Total Pressure

(Page 1 of 4)

| Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) |
|-----------|----------------|-----------|----------------|------------|----------------|------------|----------------|-----------|----------------|
| | | 4/12/2004 | 108.2 | 8/16/2004 | 123.2 | 12/20/2004 | 133.6 | 4/25/2005 | 135.0 |
| | | 4/19/2004 | 108.4 | 8/23/2004 | 124.0 | 12/27/2004 | 134.0 | 5/2/2005 | 135.4 |
| | | 4/26/2004 | 109.2 | 8/30/2004 | 124.6 | 1/3/2005 | 134.4 | 5/9/2005 | 135.6 |
| | | 5/3/2004 | 111.6 | 9/6/2004 | 125.2 | 1/10/2005 | 134.8 | 5/16/2005 | 136.0 |
| 1/5/2004 | 82.0 | 5/10/2004 | 112.7 | 9/13/2004 | 125.9 | 1/17/2005 | 135.4 | 5/23/2005 | 136.5 |
| 1/12/2004 | 85.7 | 5/17/2004 | 113.8 | 9/20/2004 | 126.6 | 1/24/2005 | 129.5 | 5/30/2005 | 136.7 |
| 1/19/2004 | 88.6 | 5/24/2004 | 114.8 | 9/27/2004 | 127.2 | 1/31/2005 | 129.8 | 6/6/2005 | 137.2 |
| 1/26/2004 | 91.7 | 5/31/2004 | 115.7 | 10/4/2004 | 127.8 | 2/7/2005 | 130.7 | 6/13/2005 | 137.5077 |
| 2/2/2004 | 93.8 | 6/7/2004 | 116.9 | 10/11/2004 | 128.5 | 2/14/2005 | 130.7 | 6/20/2005 | 137.808 |
| 2/9/2004 | 96.0 | 6/14/2004 | 116.2 | 10/18/2004 | 129.0 | 2/21/2005 | 130.8 | 6/27/2005 | 137.9852 |
| 2/16/2004 | 96.7 | 6/21/2004 | 117.0 | 10/25/2004 | 129.5 | 2/28/2005 | 131.2 | 7/4/2005 | 138.017 |
| 2/23/2004 | 98.3 | 6/28/2004 | 118.0 | 11/1/2004 | 130.1 | 3/7/2005 | 132.1 | 7/11/2005 | 138.3398 |
| 3/1/2004 | 99.9 | 7/5/2004 | 118.9 | 11/8/2004 | 130.5 | 3/14/2005 | 132.5 | 7/18/2005 | 138.6053 |
| 3/8/2004 | 101.2 | 7/12/2004 | 119.6 | 11/15/2004 | 130.8 | 3/21/2005 | 133.0 | 7/25/2005 | 139.0426 |
| 3/15/2004 | 102.8 | 7/19/2004 | 120.4 | 11/22/2004 | 131.6 | 3/28/2005 | 133.4 | 8/1/2005 | 139.2942 |
| 3/22/2004 | 104.5 | 7/26/2004 | 121.1 | 11/29/2004 | 132.2 | 4/4/2005 | 133.9 | 8/8/2005 | 139.4923 |
| 3/29/2004 | 105.6 | 8/2/2004 | 121.9 | 12/6/2004 | 132.7 | 4/11/2005 | 134.1 | 8/15/2005 | 139.7683 |
| 4/5/2004 | 106.5 | 8/9/2004 | 122.6 | 12/13/2004 | 133.3 | 4/18/2005 | 134.7 | 8/22/2005 | 139.9611 |

Appendix 2: Gas Generation - Total Pressure

(Page 2 of 4)

| Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) |
|------------|----------------|-----------|----------------|-----------|----------------|------------|----------------|-----------|----------------|
| 8/29/2005 | 138.8533 | 1/2/2006 | 143.41 | 5/8/2006 | 145.26 | 9/11/2006 | 149.02 | 1/15/2007 | 148.0188 |
| 9/5/2005 | 139.3352 | 1/9/2006 | 143.74 | 5/15/2006 | 145.39 | 9/18/2006 | 149.15 | 1/22/2007 | 148.1267 |
| 9/12/2005 | 139.6094 | 1/16/2006 | 144.09 | 5/22/2006 | 145.74 | 9/25/2006 | 149.32 | 1/29/2007 | 148.2243 |
| 9/19/2005 | 139.7 | 1/23/2006 | 144.19 | 5/29/2006 | 146.28 | 10/2/2006 | 149.48 | 2/5/2007 | 148.7116 |
| 9/26/2005 | 140.0873 | 1/30/2006 | 144.01 | 6/5/2006 | | 10/9/2006 | 149.66 | 2/12/2007 | 148.7935 |
| 10/3/2005 | 140.146 | 2/6/2006 | 144.42 | 6/12/2006 | 146.79 | 10/16/2006 | 149.74 | 2/19/2007 | 148.8478 |
| 10/10/2005 | 140.151 | 2/13/2006 | 144.86 | 6/19/2006 | 147.05 | 10/23/2006 | 149.52 | 2/26/2007 | 149.1533 |
| 10/17/2005 | 140.32 | 2/20/2006 | 144.88 | 6/26/2006 | 147.23 | 10/30/2006 | 146.452 | 3/5/2007 | 149.3409 |
| 10/24/2005 | 140.47 | 2/27/2006 | 144.81 | 7/3/2006 | 147.37 | 11/6/2006 | 146.7452 | 3/12/2007 | 149.558 |
| 10/31/2005 | 140.63 | 3/6/2006 | | 7/10/2006 | 147.28 | 11/13/2006 | 146.9329 | 3/19/2007 | 149.7335 |
| 11/7/2005 | 141.18 | 3/13/2006 | | 7/17/2006 | 147.37 | 11/20/2006 | 133.3304 | 3/26/2007 | 149.876 |
| 11/14/2005 | 141.46 | 3/20/2006 | | 7/24/2006 | | 11/27/2006 | 147.0795 | 4/2/2007 | 149.939 |
| 11/21/2005 | 142.02 | 3/27/2006 | | 7/31/2006 | 147.80 | 12/4/2006 | 147.2861 | 4/9/2007 | 150.1024 |
| 11/28/2005 | 142.21 | 4/3/2006 | | 8/7/2006 | 147.91 | 12/11/2006 | 147.2971 | 4/16/2007 | 150.025 |
| 12/5/2005 | 142.33 | 4/10/2006 | | 8/14/2006 | 147.77 | 12/18/2006 | 147.5679 | 4/23/2007 | 150.2611 |
| 12/12/2005 | 142.58 | 4/17/2006 | 146.37 | 8/21/2006 | 148.07 | 12/25/2006 | 147.7278 | 4/30/2007 | 150.4505 |
| 12/19/2005 | 142.74 | 4/24/2006 | 144.62 | 8/28/2006 | 148.54 | 1/1/2007 | 147.7405 | 5/7/2007 | 150.4635 |
| 12/26/2005 | 143.20 | 5/1/2006 | 144.94 | 9/4/2006 | 148.85 | 1/8/2007 | 147.8138 | | |

Appendix 2: Gas Generation - Total Pressure

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| Date | Pressure (kPa) |
|-------------|---------------------------|
| 5/21/2007 | 150.8699 |
| 5/28/2007 | 151.0228 |
| 6/4/2007 | 151.3127 |
| 6/11/2007 | 151.308 |
| 6/18/2007 | 151.4073 |
| 6/25/2007 | 151.5275 |
| 7/2/2007 | 151.9403 |

Appendix 2: Gas Generation - Total Pressure

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129A

| Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) | Date | Pressure (kPa) |
|------------|----------------|-----------|----------------|------------|----------------|------------|----------------|-----------|----------------|
| 10/24/2005 | 88.01 | 4/10/2006 | | 8/14/2006 | 150.10 | 12/18/2006 | 144.2387 | 4/23/2007 | 139.8767 |
| 10/31/2005 | 145.14 | 4/17/2006 | | 8/21/2006 | 149.51 | 12/25/2006 | 129.1483 | 4/30/2007 | 121.9559 |
| 11/7/2005 | 143.56 | 4/24/2006 | | 8/28/2006 | | 1/1/2007 | 144.0077 | 5/7/2007 | 120.4719 |
| 11/14/2005 | 157.43 | 5/1/2006 | | 9/4/2006 | 149.05 | 1/8/2007 | 143.7276 | 5/14/2007 | 119.7727 |
| 11/21/2005 | 157.33 | 5/8/2006 | | 9/11/2006 | 148.41 | 1/15/2007 | 144.0054 | 5/21/2007 | 119.633 |
| 11/28/2005 | 157.73 | 5/15/2006 | | 9/18/2006 | 148.05 | 1/22/2007 | 143.753 | 5/28/2007 | 119.1831 |
| 12/5/2005 | 158.95 | 5/22/2006 | 157.76 | 9/25/2006 | 148.39 | 1/29/2007 | 143.6375 | 6/4/2007 | 119.5475 |
| 12/12/2005 | 160.53 | 5/29/2006 | 157.11 | 10/2/2006 | 148.03 | 2/5/2007 | 143.4995 | 6/11/2007 | 119.7995 |
| 12/19/2005 | 160.65 | 6/5/2006 | 156.81 | 10/9/2006 | 147.68 | 2/12/2007 | 143.19 | 6/18/2007 | 120.0633 |
| 12/26/2005 | 160.90 | 6/12/2006 | 155.02 | 10/16/2006 | 147.38 | 2/19/2007 | 143.776 | 6/25/2007 | 120.2405 |
| 1/2/2006 | 161.26 | 6/19/2006 | 153.68 | 10/23/2006 | 147.17 | 2/26/2007 | 143.832 | 7/2/2007 | 120.4091 |
| 1/9/2006 | 161.60 | 6/26/2006 | 153.22 | 10/30/2006 | 147.22 | 3/5/2007 | 143.9556 | 7/9/2007 | 120.6037 |
| 1/16/2006 | 161.89 | 7/3/2006 | 152.68 | 11/6/2006 | 146.68 | 3/12/2007 | 143.4105 | 7/16/2007 | 120.9229 |
| 1/23/2006 | 161.97 | 7/10/2006 | | 11/13/2006 | 146.63 | 3/19/2007 | 142.46 | 7/23/2007 | 121.0794 |
| 1/30/2006 | 161.27 | 7/17/2006 | 151.67 | 11/20/2006 | 146.58 | 3/26/2007 | 141.96 | 7/30/2007 | 120.7284 |
| 2/6/2006 | 160.80 | 7/24/2006 | 151.54 | 11/27/2006 | 143.37 | 4/2/2007 | 141.9814 | 8/6/2007 | 120.8242 |
| 2/13/2006 | 160.71 | 7/31/2006 | 151.12 | 12/4/2006 | 144.20 | 4/9/2007 | 141.5801 | | |
| 2/20/2006 | 161.03 | 8/7/2006 | 150.54 | 12/11/2006 | 144.45 | 4/16/2007 | 139.9558 | | |

Appendix 3: Estimating the monolayer coverage

(Page 1 of 2)

Surface Area: The number of monolayers of moisture on the sample surface may be calculated if the mass of moisture or water, the mass of the sample, and the SSA of the sample are known. One approach is to determine the weight percentage for one monolayer of water. The number of monolayers of water can be calculated by dividing the total weight percentage of water (mass of water/mass of the sample) by the weight percentage of one monolayer of water.¹³ The weight percentage of one monolayer of water is the product of the weight of water in a monolayer of 1 m² and the SSA:

$$\text{wt\% of 1 ML} = 0.00022 \text{ g m}^{-2}\text{ML}^{-1} \times \text{SSA m}^2 \text{ g}^{-1} \times 100 \text{ wt\%} = 0.022 \text{ wt\% ML}^{-1} \times \text{SSA}$$

Equation A3-1

For the material in SSR129 with a SSA of 3.18 m² g⁻¹, the weight percentage of one monolayer of water is 0.070 wt% ML⁻¹. For the material in SSR129A with a SSA of 0.67 m² g⁻¹, the weight percentage of one monolayer of water is 0.015 wt% ML⁻¹.

Dividing the weight percentage of water by the weight percentage of water in one monolayer yields the number of monolayers of water. Applying this to the measured weight percentage of water upon loading and unloading results in the values summarized below:

| | Estimated total moisture in loaded sample from Table 5 | |
|--------------|--|---------------|
| | SSR 129 (TGA) | SSR129A (LOI) |
| Wt% Moisture | 0.82 | 0.35 |
| ML | 11.7 | 23.3 |

Appendix 3: Estimating the monolayer coverage

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BET Theory: The number of monolayers can also be estimated based upon the relative humidity in the container using Brunauer-Emmett-Teller (BET) theory.¹¹ BET theory is the standard model for quantifying the equilibria between multiple physically adsorbed layers on a surface and the adsorbing species in the gas above the surface. The specific relationship between the RH above a surface and the number of monolayers of weakly bound water on the surface predicted by BET theory is illustrated in Fig. A3-1.

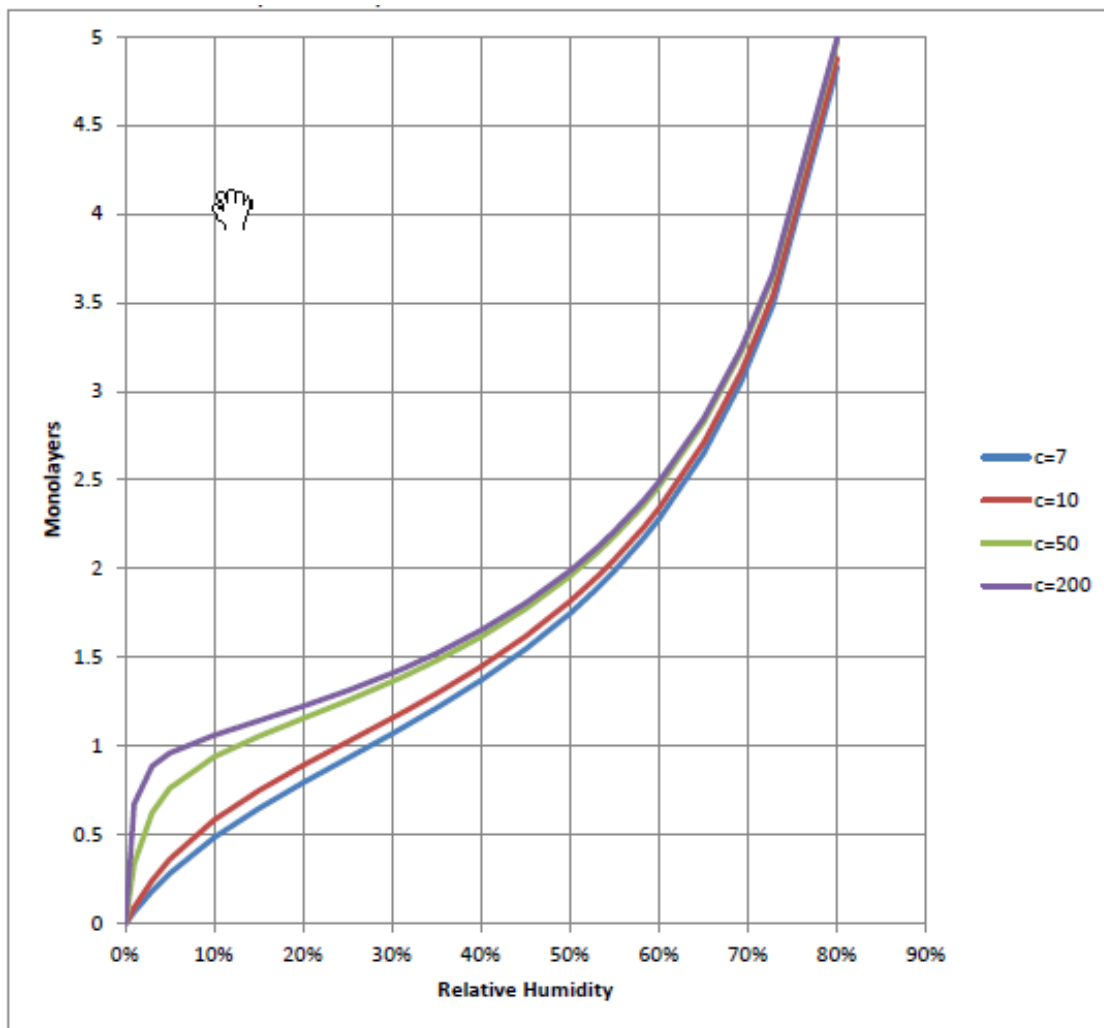


Figure A3-1. Adsorption Isotherm Calculated from BET Theory.

The equation for calculating the number of monolayers at a given RH and c value is given in Equation A3-2.

$$c \cdot RH/100 / (1 - RH/100) [1 + (c-1)RH/100]$$

Equation A3-2

Appendix 4: Stopping power ratio

(Page 1 of 1)

The ratio of the stopping power due to the water and the stopping power due to the material in SSR129 is calculated using the approach in Appendix B of Reference 6. Elements with greater than 0.3 wt% were included.

| Element or Compound | Integrated Stopping Power from 0 to 5.2 MeV ($\text{mg}^{-1} \text{cm}^{-2}$) | Elemental Mass Fraction | Elemental Stopping Power ($\text{mg}^{-1} \text{cm}^{-2}$) |
|----------------------|---|-------------------------|--|
| H ₂ O(g) | 7.946 | 0.0000 | 0 |
| H ₂ O (l) | 7.708 | 0.0082 | 0.063202 |
| F | 6.645 | | 0 |
| O | 5.901 | 0.0021 | 0.012569 |
| Na | 5.304 | | |
| C | 5.190 | | 0 |
| S | 5.117 | 0.0043 | 0.022206 |
| Mg | 5.100 | 0.0000 | 0 |
| Si | 4.852 | 0.0000 | |
| Al | 4.702 | 0.0000 | 0 |
| K | 4.652 | | |
| Cl | 4.575 | | 0 |
| Ca | 4.461 | | 0 |
| Cr | 3.688 | | 0 |
| Fe | 3.504 | | |
| Ni | 3.184 | 0.0424 | 0.135006 |
| Cu | 2.871 | | 0 |
| Zn | 2.860 | | 0 |
| Ga | 2.786 | 0.0096 | 0.026631 |
| UO ₂ | 2.081 | 0.9379 | 1.95 |
| PuO ₂ | 2.081 | 0.0000 | 0 |
| | | Smat | 2.157 |
| | | Swat | 7.708 |
| | | S | 3.57 |

Appendix 5: Obtaining G-values and rate constants

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As discussed in the H₂ G-value section, a three exponential function (Eq. 5) was used to fit the time dependence of the partial pressure curve for hydrogen for SSR129. The function has fitting parameters, A₀, the initial water involved in hydrogen generation and k₁ the hydrogen formation rate constant can be used along with information of material properties and container geometry to calculate the initial rate, the hydrogen G-value. This appendix documents the methodology for obtaining this information.

Calculation of G(H₂)

G(H₂) can be calculated by equating the initial rate of hydrogen generation to the product of the rate of dose to the water and G(H₂),

$$\frac{dN_{H_2}}{dt} = \dot{D}_{H_2O} G(H_2) \quad \text{Equation A5-1}$$

where N_{H2} is the number of molecules of hydrogen and \dot{D}_{H_2O} is the rate of adsorbed dose to the water with units eV s⁻¹. The initial rate evaluated at time zero in units of molecules per second rather than kPa per day, given P_{H2} is zero at t = 0.

$$\begin{aligned} \left. \frac{dP}{dt} \right|_{t=0} &= k_1 A_0 \\ \frac{dN_{H_2}}{dt} &= \frac{dP}{dt} \frac{V_g N_A}{R T} = k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} \\ k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} &= \dot{D}_{H_2O} G(H_2) \end{aligned} \quad \text{Equation A5-2}$$

In Equation A5-2, V_g is the gas volume within the reactor, N_A is Avogadro's number, R is the universal gas constant, T is the temperature in the gas phase during the time the data was collected. The method for calculating V_g within an SSR is shown in the Loading section. The dose rate to the water is given by

Appendix 5: Obtaining G-values and rate constants

(Page 2 of 2)

$$\begin{aligned}\dot{D}_{H_2O} &= P_{mat} \frac{6.2418 \times 10^{18} \text{ eV}}{\text{s W}} m_{mat} f_{H_2O} \frac{S_{H_2O}}{S_{mat}} \\ f_{H_2O} &= \frac{m_{H_2O}}{m_{mat}} \\ \dot{D}_{H_2O} &= P_{mat} \frac{6.2418 \times 10^{18} \text{ eV}}{\text{s W}} m_{H_2O} \frac{S_{H_2O}}{S_{mat}}\end{aligned}\quad \text{Equation A5-3}$$

where P_{mat} is the specific power of the material in W g^{-1} , m_{mat} is the mass of the material, f_{H_2O} is the fraction of water, and the ratio S_{H_2O}/S_{mat} is the ratio of the stopping power of alpha particles in water to the stopping power in the material. An approach for calculating S_{H_2O}/S_{mat} is given in Appendix B. For high-purity plutonium dioxide with adsorbed water and no impurities the ratio S_{H_2O}/S_{mat} for 5.2 MeV α -particles is ~ 3.70 . Combining Equation A5-2 and A5-3 yields a general expression for $G(H_2)$ using the fitting parameters a and b, and the material properties,

$$G(H_2) = k_1 A_0 \frac{V_g N_A}{R T} \frac{\text{day}}{86400 \text{ s}} \frac{1}{P_{mat} \frac{6.2418 \times 10^{18} \text{ eV}/100}{\text{s W}} m_{H_2O}} \frac{1}{\frac{S_{H_2O}}{S_{mat}}} \cdot \quad \text{Equation A5-4}$$

Appendix 6: Symbols and Conversion Factors

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Symbols

| Symbol | Units | Description |
|-------------|---|---|
| A | kPa | Water involved in hydrogen generation |
| A_0 | kPa | Initial water involved in hydrogen gen (fitting parameter) |
| k_1 | day ⁻¹ | Rate constant for the formation of hydrogen from water (fitting parameter) |
| k_2 | day ⁻¹ | Rate constant for the consumption of hydrogen (fitting parameter) |
| k_3 | day ⁻¹ | Rate constant for the back reaction formation of hydrogen (fitting parameter) |
| \dot{D}_x | eV s ⁻¹ or J s ⁻¹ or W | Rate of adsorbed dose to x |
| $G(x)$ | molecules 100 eV ⁻¹ | Number of molecules of x produced per 100 eV of adsorbed dose |
| f_x | --- | Fraction of material x in the total material |
| m_x | g | Mass of x |
| N_x | molecules | Number of molecules of substance x |
| N_A | molecules mol ⁻¹ | Avogadro's number |
| p_x | kPa | Partial pressure of x |
| P_x | W g ⁻¹ or eV s ⁻¹ g ⁻¹ | Specific power of x |
| S_x | m | Stopping power of x to alpha radiation |
| SSA | m ² g ⁻¹ | Specific Surface Area of the material |
| t | s or day or yr | Time |
| T | K | Temperature |
| V_g | cm ³ | Volume that the gas occupies |

Appendix 6: Symbols and Conversion Factors

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Unit conversions

| | |
|-------|---|
| 1 W | $6.2418 \times 10^{18} \text{ eV s}^{-1}$ |
| 1 day | 86400 s |
| 1 day | 24 hr |
| N_A | $6.0221367 \times 10^{23} \text{ molecules mol}^{-1}$ |
| R | $8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$ $8.314510 \text{ kPa L mol}^{-1} \text{ K}^{-1}$ $8314.510 \text{ kPa cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ |